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# Reversible Photoreduction of Cu(II)-Coumarin Metal-Organic Polyhedra

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### Part S1. General Information

#### 1. Materials

Copper (II) acetate monohydrate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ), 1,2-dibromoethane and copper (I) chloride ( $\text{CuCl}$ ) were bought from Sigma Aldrich. 1,3-Dibromopropane, 1,6-dibromohexane, 7-hydroxycoumarin, dimethyl 5-hydroxyiso-phthalate, acetonitrile anhydrous, chloroform-*d*, copper (I) iodide ( $\text{CuI}$ ), and *N,N*-dimethylformamide (DMF) were purchased from Alfa Aesar Chemicals. Benzophenone and *N,N*-diethylformamide (DEF) was bought from Tokyo Chemical Industry Co., LTD. Potassium carbonate anhydrous, sodium hydroxide beads ( $\text{NaOH}$ ), magnesium sulfate anhydrous ( $\text{MgSO}_4$ ), ethyl alcohol anhydrous ( $\text{EtOH}$ ), acetone, dichloromethane (DCM), ethyl acetate (EA), chloroform, tetrahydrofuran (THF) and methyl alcohol anhydrous ( $\text{MeOH}$ ) were purchased from Daejung Chemicals. Hydrochloric acid ( $\text{HCl}$ ) was bought from WAK Chemicals and dimethylsulfoxide-*d*<sub>6</sub> was bought from Euriso-top.

#### 2. Measurements

UV-Vis spectra were recorded on SHIMADZU spectrometer (UV-2600). Hydrogen nuclear magnetic resonance ( $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR) spectra were measured on Fourier transform nuclear magnetic resonance spectrometer from Bruker (AVANCE III 400). Chemical shifts are reported in ppm downfield in the NMR solvent ( $\text{CDCl}_3$ -*d*<sub>1</sub>:  $\delta$  7.24, and  $\text{DMSO}$ -*d*<sub>6</sub>:  $\delta$  2.50). FT-IR spectra were collected by Fourier transform infrared spectrometer from Thermo Scientific (Nicolet 6700). Thermogravimetric analyzer (TGA) data were obtained by TA Instruments (Auto Q500) with a heating rate of 5 °C/min. Elementary analysis was performed on Elementar (Vario Micro Cube). TEM images were figured by Titan Themis (FEI) electron microscope operating at 80 kV. Atomic force microscopy (AFM) images were collected using NX10 (Park System). For the light source of the MOP reduction experiments, the UV lamp (LF-215.LS, 15 watts, 365 nm) from UVITEC Cambridge was used. Dynamic Light Scattering (DLS) data was collected by Malvern Instruments (ZEN36000).

## 1. Synthesis of Organic Ligands

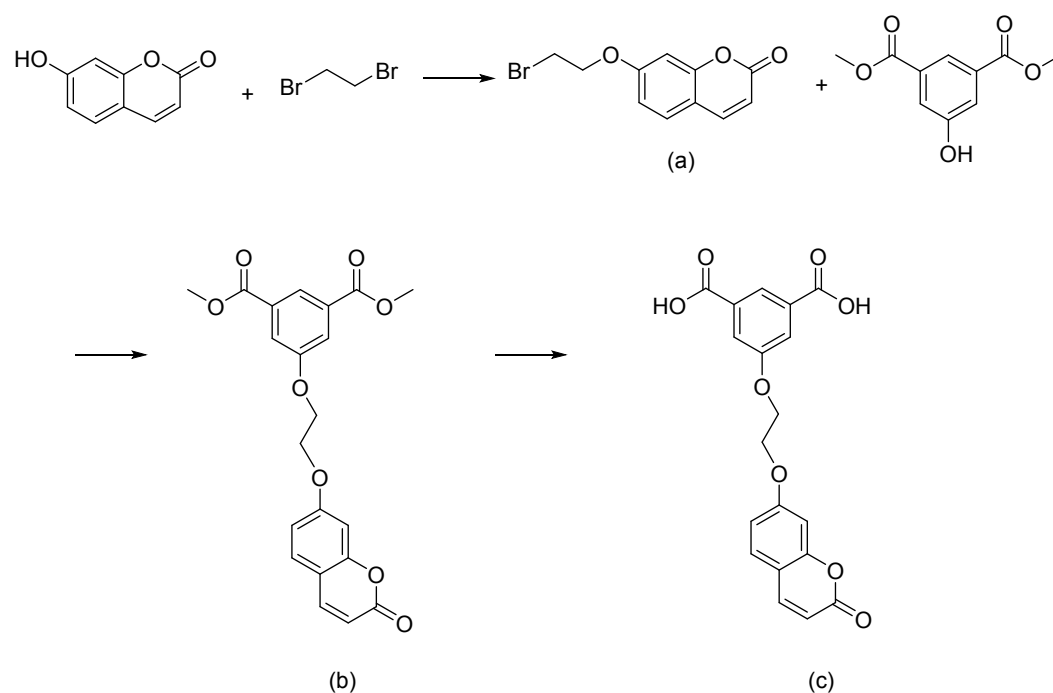


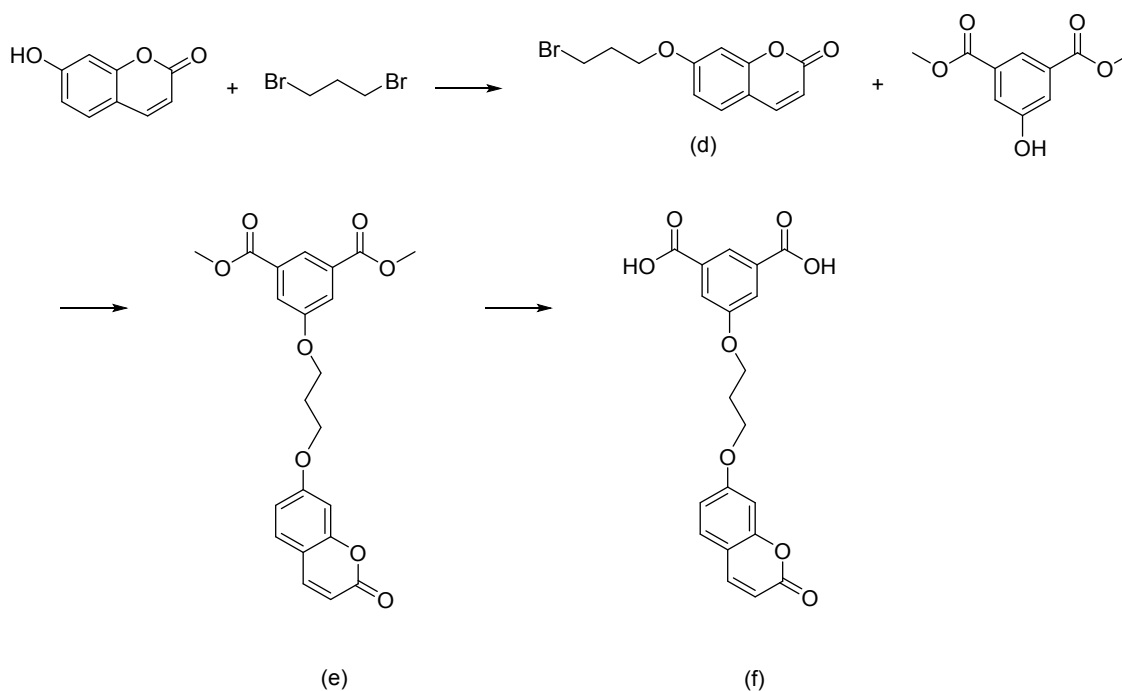
Figure S1. Synthesis of L1.

**L1:** Potassium carbonate (5.528 g, 40.0 mmol), 1,2-dibromoethane (37.572 g, 200 mmol) and 7-hydroxycoumarin (3.243g, 20.0 mmol) were added to 60 ml of acetone. The reaction mixture was refluxed for 12 h. After removing potassium carbonate by filtration, the solvent was concentrated under vacuum. The residue was dissolved in DCM and then the water (100 ml) was added. The aqueous phase was extracted three times with DCM. The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated under vacuum to yield 7-(2-bromoethoxy)coumarin (4.571 g, 16.98 mmol, 84.9% yield) **(a)**.  $^1\text{H-NMR}$  (400MHz;  $\text{CDCl}_3-d_1$ ):  $\delta$  7.58 (d, 1H,  $J=12$  Hz), 7.36 (d, 1H,  $J=8$  Hz), 6.860 (d, 1H,  $J=2.8$  Hz), 6.82 (q, 1H,  $J=12, 8$  Hz), 6.24 (d, 1H,  $J=8$  Hz), 4.35 (t, 2H,  $J=8, 4$  Hz), 3.62 (t, 2H,  $J=8, 4$  Hz).

Potassium carbonate (2.421 g, 17.5 mmol), dimethyl 5-hydroxyiso-phthalate (3.393 g, 16.1 mmol) and 7-(2-bromoethoxy)coumarin (4.571 g, 16.1 mmol) were added to 80 ml of dry acetonitrile and then the reaction mixture was refluxed for 12 h. After removing potassium carbonate by filtration, the solvent was concentrated under vacuum. The residue was dissolved in chloroform and then water (100 ml) was added. The aqueous phase was extracted three times with chloroform. The combined organic layers were dried over  $\text{MgSO}_4$ . The clear solution was purified by fresh column chromatography with ethyl acetate as an eluent. The concentrated residue under vacuum was washed with acetone to yield 7-(2-(1,3-dimethyl 5-isophthalate)ethoxy)coumarin (2.34 g, 5.88 mmol, 36.4% yield) **(b)**.  $^1\text{H-NMR}$  (400MHz;  $\text{CDCl}_3-d_1$ ):  $\delta$  8.30 (s, 1H), 7.80 (s, 2H), 7.63 (d, 1H,  $J=8$  Hz), 7.38 (d, 1H,  $J=8$  Hz), 6.891 (d, 1H,  $J=2$  Hz), 6.86 (q, 1H,  $J=12, 8$  Hz), 6.25 (d, 1H,  $J=12$  Hz), 4.42 (q, 4H,  $J=16, 12$  Hz), 3.92 (s, 6H). 7-(2-(1,3-dimethyl 5-isophthalate)ethoxy)coumarin (2.341 g, 5.87 mmol) was dissolved in a 195 ml mixture of THF and MeOH (1:1), to which a solution of NaOH (9.39 g, 235 mmol) in 98 ml of water was added. The mixture was refluxed for 12 h. Upon completion, THF and MeOH were evaporated. The solution was then acidified with 1 M HCl until no further precipitate was formed. The precipitate was collected by filtration, washed with water, and dried in an oven to yield **L1** (white powder, 2.064 g, 5.58 mmol, 94.9% yield) **(c)**.  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO}-d_6$ ):  $\delta$

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13.01 (br, 2H), 8.10 (t, 1H,  $J=4$  Hz), 7.96 (d, 1H,  $J=12$  Hz), 7.70 (d, 2H,  $J=1.6$  Hz), 7.63 (d, 1H,  $J=8$  Hz), 7.04 (d, 1H,  $J=2.4$  Hz), 7.00 (q, 1H,  $J=8$  Hz), 6.27 (d, 1H,  $J=12$  Hz), 4.48 (s, 4H).  $^{13}\text{C}$  NMR (400 MHz;  $\text{DMSO}-d_6$ ):  $\delta$  166.78, 161.90, 160.66, 158.94, 155.85, 144.66, 133.22, 129.99, 123.05, 119.78, 113.19, 113.14, 113.09, 101.97, 67.62, 67.41. FT-IR ( $\nu$  max): 3070, 2810, 2520, 2360, 1735, 1688, 1592, 562, 1513, 1454, 1428, 1399, 1273, 1231, 1199, 1127, 1056, 997, 965, 891, 865, 829, 754, 688, 663  $\text{cm}^{-1}$ . Elemental analysis (%calc/found): C, 60.77/61.52; H, 3.83/3.966.



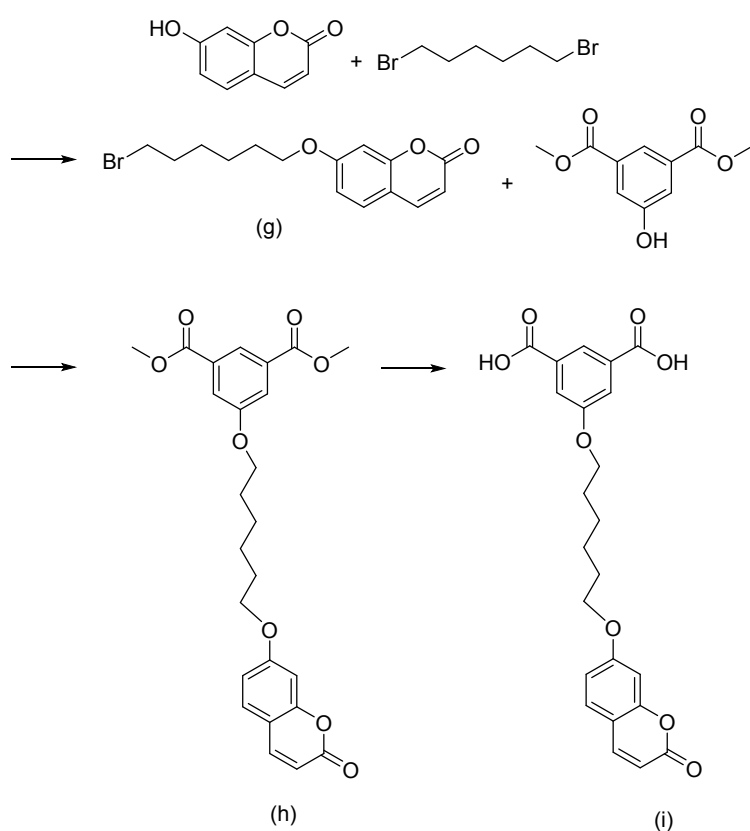
**Figure S2.** Synthesis of L2.

**L2:** Potassium carbonate (39.8 g, 288 mmol), 1,3-dibromopropane (40.378 g, 200 mmol) and 7-hydroxycoumarin (3.243 g, 20.0 mmol) were added to 200 ml of acetone. The reaction mixture was refluxed for 12 h. After removing potassium carbonate by filtration, the solvent was concentrated under vacuum. The residue was dissolved in DCM and then water (100 ml) was added. The aqueous phase was extracted three times with DCM. The combined organic layers dried over  $\text{MgSO}_4$  and the concentrated under vacuum to yield 7-(3-bromopropoxy)coumarin (6.011 g, 21.2 mmol, 100% yield) (d).  $^1\text{H}$ -NMR (400MHz;  $\text{CDCl}_3-d_1$ ):  $\delta$  7.58 (d, 1H,  $J=8$  Hz), 7.34 (d, 1H,  $J=8$  Hz), 6.83 (d, 1H,  $J=4$  Hz), 6.82 (q, 1H,  $J=4$  Hz), 6.23 (d, 1H,  $J=12$  Hz), 4.18 (t, 2H,  $J=8, 4$  Hz), 3.57 (t, 2H,  $J=8, 4$  Hz), 2.35 (m, 2H,  $J=16, 12$  Hz).

Potassium carbonate (1.938 g, 14.0 mmol), dimethyl 5-hydroxyisophthalate (2.716 g, 12.9 mmol) and 7-(3-bromopropoxy)coumarin (5.487 g, 19.4 mmol) were added to 65 ml of dry acetonitrile and then the reaction mixture was refluxed for 12 h. After removing potassium carbonate by filtration, the solvent was concentrated under vacuum. The residue was dissolved in chloroform and then water (100 ml) was added. The aqueous phase was extracted three times with chloroform. The combined organic layers were dried over  $\text{MgSO}_4$ . The clear solution was purified by fresh column chromatography with ethyl acetate as an eluent. The concentrated residue under vacuum was washed with acetone to yield 7-(3-(1,3-dimethyl 5-isophthalate)propoxy)coumarin (3.809 g, 9.24 mmol, 71.9% yield) (e).  $^1\text{H}$ -NMR (400MHz;  $\text{CDCl}_3-d_1$ ):  $\delta$  8.26 (t, 1H), 7.74 (d, 2H,  $J=4$  Hz), 7.61 (d, 1H,  $J=8$  Hz), 7.35 (d, 1H,  $J=8$  Hz), 6.84 (d, 1H,  $J=4$  Hz), 6.82 (s, 1H), 6.23 (d, 1H,  $J=8$  Hz), 4.23 (m, 4H,  $J=12$  Hz), 3.92 (s, 6H), 2.32 (m, 2H,  $J=16, 2$  Hz).

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7-(3-(1,3-dimethyl 5-isophthalate)propyloxy)coumarin (3.809 g, 9.24 mmol) was dissolved in a 300 ml mixture of THF and MeOH (1:1), to which a solution of NaOH (14.778 g, 370 mmol) in 150 ml of water was added. The mixture was refluxed for 12 h. Upon completion, THF and MeOH were evaporated. The solution was then acidified with 1M HCl until no further precipitate was formed. The precipitate was collected by filtration, washed with water, and dried in an oven to yield **L2**. (white powder, 2.860 g, 7.44 mmol, 80.57% yield) (**f**).  $^1\text{H-NMR}$  (400MHz;  $\text{DMSO-}d_6$ ):  $\delta$  13.31 (br, 2H), 8.07 (t, 1H,  $J=4$  Hz), 7.98 (d, 1H,  $J=12$  Hz), 7.67 (d, 2H), 7.62 (d, 1H,  $J=8$  Hz), 7.031 (d, 1H,  $J=2$  Hz), 6.98 (q, 1H,  $J=4$  Hz), 6.28 (d, 1H,  $J=8$  Hz), 4.27 (m, 4H,  $J=12, 8$  Hz), 2.23 (m, 2H,  $J=12$  Hz).  $^{13}\text{C NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ):  $\delta$  166.81, 162.16 160.68, 159.09, 155.88, 144.67, 133.16, 129.92, 122.81, 119.62, 113.0, 112.97, 112.90, 101.85, 65.56, 65.38, 28.81. FT-IR ( $\nu$  max): 3065, 2821, 2545, 1680, 1590, 1510, 1460, 1430, 1400, 1282, 1230, 1207, 1120, 1050, 1025, 1005, 984, 924, 895, 876, 863, 835, 752, 695, 661  $\text{cm}^{-1}$ . Elemental analysis (%calc/found): C, 61.69/61.79; H, 4.24/4.393.



**Figure S3.** Synthesis of **L3**.

**L3:** Potassium carbonate (1.659 g, 12.0 mmol), 1,6-dibromohexane (3.381 g, 18.0 mmol) and 7-hydroxycoumarin (0.973 g, 6.00 mmol) were added to 30 ml of acetone. The reaction mixture was refluxed for 12 h. After removing potassium carbonate by filtration, the solvent was concentrated under vacuum. The residue was dissolved in DCM and then water (100 ml) was added. The aqueous phase was extracted three times with DCM. The combined organic layers dried over  $\text{MgSO}_4$  and then concentrated under vacuum. The residue was washed by MeOH. Yield 7-(6-bromohexyloxy)coumarin (1.173 g, 3.60 mmol, 60.1% yield) (**g**).  $^1\text{H-NMR}$  (400 MHz;  $\text{CDCl}_3-d_1$ ):  $\delta$  7.61 (d, 1H,  $J=12$  Hz), 7.34 (d, 1H,  $J=8$  Hz), 6.82 (d, 1H,  $J=4$  Hz), 6.79 (q, 1H,  $J=12, 8$  Hz), 6.22 (d, 1H,  $J=12$  Hz), 4.02 (t, 3H,  $J=8, 4$  Hz), 1.85 (t, 3H,  $J=8, 4$  Hz), 1.53 (s, 6H). Potassium carbonate (0.997 g, 7.21 mmol), Dimethyl 5-hydroxyiso-phthalate (0.758 g, 3.60 mmol) and 7-(6-bromohexyloxy)coumarin (1.173 g, 3.60 mmol) were added in 30 ml of dry acetonitrile and then the reaction mixture was refluxed for 12 h. After removing potassium carbonate by filtration, the solvent was concentrated under vacuum. The residue was dissolved

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in chloroform and then the water (100 ml) was added. The aqueous phase was extracted three times with chloroform. The combined organic layers were dried over  $\text{MgSO}_4$ . The clear solution was purified by fresh column chromatography with ethyl acetate as an eluent. The concentrated residue under vacuum was washed with acetone to yield 7-(6-(1,3-dimethyl 5-isophthalate)hexyloxy)coumarin (0.35 g, 0.77 mmol, 21.39% yield) (**h**).  $^1\text{H-NMR}$  (400 MHz;  $\text{CDCl}_3-d_1$ ):  $\delta$  8.26 (t, 1H, J= 4 Hz), 7.74 (d, 2H, J= 4 Hz), 7.61 (d, 1H, J= 8 Hz), 7.35 (d, 1H, J= 8 Hz), 6.84 (d, 1H J= 4 Hz), 6.82 (s, 1H), 6.23 (d, 1H, J= 8 Hz), 4.23 (m, 5H, J= 12 Hz), 3.92 (s, 7H), 2.94 (s, 2H), 2.86 (s, 1H), 2.31 (t, 2H, J= 8, 4 Hz).

7-(6-(1,3-dimethyl 5-isophthalate)hexyloxy)coumarin (0.35 g, 0.77 mmol) was dissolved in a 30ml mixture of THF and MeOH (1:1), to which a solution of NaOH (1.232 g, 30.8 mmol) in 15 ml of water was added. The mixture was refluxed for 12 h. Upon completion, THF and MeOH were evaporated. The solution was then acidified with 1 M HCl until no further precipitate was formed. The precipitate was collected by filtration, washed with water, and dried in an oven to yield **L3** (white powder, 0.182 g, 0.427 mmol, 55.49% yield) (**i**).  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO}-d_6$ ):  $\delta$  13.27 (br, 2H), 8.07 (t, 1H), 7.98 (d, 1H, J= 12 Hz), 7.67 (d, 2H, J= 1.2 Hz), 7.62 (d, 1H, J= 8 Hz), 7.029 (d, 1H, J= 2.4 Hz), 6.98 (q, 1H, J= 8 Hz), 6.28 (d, 1H, J= 8 Hz), 4.27 (m, 4H, J=12, 8 Hz), 2.23 (t, 3H, J= 8, 4 Hz), 1.23 (s, 2H).  $^{13}\text{C NMR}$  (400 MHz;  $\text{DMSO}-d_6$ ):  $\delta$  166.82, 162.17, 160.69, 159.10, 155.89, 144.71, 133.21, 129.95, 122.80, 119.61, 113.14, 112.99, 112.92, 101.87, 65.58, 65.39, 28.81. FT-IR ( $\nu$  max): 3070, 2830, 2560, 1688, 1609, 1513, 1465, 1430, 1399, 1280, 1209, 1120, 1050, 1027, 1008, 986, 895, 878, 865, 835, 755, 691, 659  $\text{cm}^{-1}$ . Elemental analysis (%calc/found): C, 62.52/61.4; H, 4.45/4.748.

### 2. Synthesis of Metal-Organic Polyhedra

**Coumarin-MOP-1:** A solution of **L1** (0.0083 g, 0.0225 mmol) in 0.5 ml of DEF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0041g, 0.0205mmol) in 0.5 ml of DEF. Blue cubic crystals of MOP-1 were obtained by ether vapour diffusion over a period of a week. FT-IR ( $\nu$  max): 1729, 1610, 1583, 1504, 1453, 1376, 1266, 1229, 1123, 1062, 985, 887, 831, 801, 773, 730  $\text{cm}^{-1}$ . Elemental analysis (%calc/found): C, 52.85/52.53; H, 2.8/4.366.

**Coumarin-MOP-2:** A solution of **L2** (0.0346 g, 0.0900 mmol) in 1 ml of DEF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0163 g, 0.0819mmol) in 0.9 ml of DEF and 0.1 ml of EtOH. Blue cubic crystals of MOP-2 were obtained by ether vapour diffusion over a period of a week. FT-IR ( $\nu$  max): 1725, 1705, 1608, 1577, 1454, 1373, 1260, 1230, 1121, 1051, 1014, 992, 885, 824, 806, 773, 727  $\text{cm}^{-1}$ . Elemental analysis (%calc/found): C, 53.88/52.56; H, 3.17/4.171.

**Coumarin-MOP-3:** A solution of **L3** (0.0096 g, 0.0225 mmol) in 0.5 ml of DEF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0041 g, 0.0205 mmol) in 0.25 ml of DEF and 0.25 ml of EtOH. Blue cubic crystals of MOP-3 were obtained by ether vapour diffusion over a period of a week. FT-IR ( $\nu$  max): 1697, 1600, 1580, 1550, 1450, 1380, 1270, 1230, 1120, 1050, 1020, 997, 885, 824, 806, 773, 727  $\text{cm}^{-1}$ . Elemental analysis (%calc/found): C, 56.61/52.33; H, 4.13/4.373.

### 3. Reduction study of Coumarin-MOPs

The MOP stock solution (27 mM against  $\text{Cu}^{2+}$ ) and benzophenone stock solution (27 mM) were diluted with additional solvent owing to make the 3 mM solution which was the appropriate concentration to obtain UV-Vis spectra of the solution. In order to make the benzophenone stock solution (27 mM against  $\text{Cu}^{2+}$ ), benzophenone (0.0148 g, 0.081 mmol) was dissolved in 3 ml of DMF.

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**Coumarin-MOP-1:** In order to make the coumarin-MOP-1 stock solution (27 mM against  $\text{Cu}^{2+}$ ), a solution of **L1** (0.0300 g, 0.081 mmol) in 1.5 ml of DMF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0162 g, 0.081 mmol) in 1.5 ml of DMF. This coumarin-MOP-1 stock solution was kept for 1 day. The 278  $\mu\text{l}$  MOP stock solution was diluted with 1.7 ml of DMF and then 278  $\mu\text{l}$  benzophenone stock solution, 125  $\mu\text{l}$  of diethyl ether, and 125  $\mu\text{l}$  of methanol were added to it. The solution was purged with Ar gas for 30 seconds and then irradiated by UV light (365 nm) with stirring.

**Coumarin-MOP-2:** In order to make the coumarin-MOP-2 stock solution (27 mM against  $\text{Cu}^{2+}$ ), a solution of **L2** (0.0311 g, 0.081 mmol) in 1.5 ml of DMF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0162 g, 0.081 mmol) in 1.5 ml of DMF. This coumarin-MOP-2 stock solution was kept for 1 day. The 278  $\mu\text{l}$  MOP stock solution was diluted with 1.7 ml of DMF and then 278  $\mu\text{l}$  benzophenone stock solution, 125  $\mu\text{l}$  of diethyl ether, and 125  $\mu\text{l}$  of methanol were added to it. The solution was purged with Ar gas for 30 seconds and then irradiated by UV light (365 nm) with stirring.

**Coumarin-MOP-3:** In order to make the coumarin-MOP-3 stock solution (27 mM against  $\text{Cu}^{2+}$ ), a solution of **L3** (0.0345 g, 0.081 mmol) in 1.5 ml of DMF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0162 g, 0.081 mmol) in 1.5 ml of DMF. This coumarin-MOP-3 stock solution was kept for 1 day. The 278  $\mu\text{l}$  MOP stock solution was diluted with 1.7 ml of DMF and then 278  $\mu\text{l}$  benzophenone stock solution, 125  $\mu\text{l}$  of diethyl ether, and 125  $\mu\text{l}$  of methanol were added to it. The solution was purged with Ar gas for 30 seconds and then irradiated by UV light (365 nm) with stirring.

### 4. Reversible $\text{Cu}^{2+}$ to $\text{Cu}^+$ reduction process

The MOP stock solution (27 mM against  $\text{Cu}^{2+}$ ) and benzophenone stock solution (27 mM) were diluted with additional solvent owing to make the 3 mM solution which was the appropriate concentration to obtain UV-Vis spectra of the solution. In order to make the benzophenone stock solution (27 mM against  $\text{Cu}^{2+}$ ), benzophenone (0.0148 g, 0.081 mmol) was dissolved in 3 ml of DMF.

**Coumarin-MOP-1:** In order to make the coumarin-MOP-1 stock solution (27 mM against  $\text{Cu}^{2+}$ ), a solution of **L1** (0.0300 g, 0.081 mmol) in 1.5 ml of DMF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0147 g, 0.081 mmol) in 1.5 ml of DMF. This coumarin-MOP-1 stock solution was kept for 1 day. The 278  $\mu\text{l}$  MOP stock solution was diluted with 1.7 ml of DMF and then 278  $\mu\text{l}$  benzophenone stock solution, 125  $\mu\text{l}$  of diethyl ether, and 125  $\mu\text{l}$  of methanol were added to it. The solution was purged with Ar gas for 30 seconds and then irradiated by UV light (365 nm) with stirring. When the blue solution became clear, air is bubble through the solution for 30 seconds. The color of the solution became blue upon the  $\text{Cu}^+$  oxidation. The UV irradiation and air exposure processes were repeated for three cycles.

**Coumarin-MOP-2:** In order to make the coumarin-MOP-2 stock solution (27 mM against  $\text{Cu}^{2+}$ ), a solution of **L2** (0.0311 g, 0.081 mmol) in 1.5 ml of DMF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0147 g, 0.081 mmol) in 1.5 ml of DMF. This coumarin-MOP-2 stock solution was kept for 1 day. The 278  $\mu\text{l}$  MOP stock solution was diluted with 1.7 ml of DMF and then 278  $\mu\text{l}$  benzophenone stock solution, 125  $\mu\text{l}$  of diethyl ether, and 125  $\mu\text{l}$  of methanol were added to it. The solution was purged with Ar gas for 30 seconds and then irradiated by UV light (365 nm) with stirring. When the blue solution became clear, air is bubble through the solution for 30 seconds. The color of the solution became blue upon the  $\text{Cu}^+$  oxidation. The UV irradiation and air exposure processes were repeated for three cycles.



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**Coumarin-MOP-3:** In order to make the coumarin-MOP-3 stock solution (27 mM against  $\text{Cu}^{2+}$ ), a solution of **L3** (0.0345 g, 0.081 mmol) in 1.5 ml of DMF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0147 g, 0.081 mmol) in 1.5 ml of DMF. This coumarin-MOP-3 stock solution was kept for 1 day. The 278  $\mu\text{l}$  MOP stock solution was diluted with 1.7 ml of DMF and then 278  $\mu\text{l}$  benzophenone stock solution, 125  $\mu\text{l}$  of diethyl ether, and 125  $\mu\text{l}$  of methanol were added to it. The solution was purged with Ar gas for 30 seconds and then irradiated by UV light (365 nm) with stirring. When the blue solution became clear, air is bubble through the solution for 30 seconds. The color of the solution became blue upon the  $\text{Cu}^+$  oxidation. The UV irradiation and air exposure processes were repeated for three cycles.

### 5. Control experiments for UV irradiation

**$\text{Cu}(\text{NO}_3)_2$ :** A solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.0022 g, 0.009 mmol) in 0.9 ml of DMF, 0.05 ml of diethyl ether and 0.05 ml of methanol. Benzophenone (0.0016 g, 0.009 mmol) was dissolved in  $\text{Cu}(\text{NO}_3)_2$  solution. The  $\text{Cu}(\text{NO}_3)_2$  solution was purged with Ar gas for 30 seconds. The solution placed with UV light at 365 nm and magnetic stirring. After UV irradiation for 40 minutes, a green precipitate was formed in solution. After additional UV irradiation for an hour, the green precipitate was changed to a brown precipitate. Finally, after UV irradiation for 1.5 h, the brown precipitate was changed to a black precipitate.

**$\text{Cu}(\text{CH}_3\text{COO})_2$ :** A solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0018 g, 0.009 mmol) in 0.9 ml of DMF, 0.05 ml of diethyl ether and 0.05 ml of methanol. Benzophenone (0.0016 g, 0.009 mmol) was dissolved in  $\text{Cu}(\text{CH}_3\text{COO})_2$  solution. The  $\text{Cu}(\text{CH}_3\text{COO})_2$  solution was purged with Ar gas for 30 seconds. The solution placed with UV light at 365 nm and magnetic stirring. After UV irradiation for 30 minutes, a green precipitate was formed in solution. After UV irradiation for an hour, the green precipitate was changed to a yellow precipitate. After additional 1.5 h, a yellow precipitate was changed to a brown precipitate. Finally, after UV irradiation for 2 h, the brown precipitate was changed to a black precipitate.

**MOP-4:** A solution of 5-tert-butylisophthalic acid (0.0020 g, 0.009 mmol) in 0.5 ml of DMF was added to a solution of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.0018 g, 0.009 mmol) in 0.4 ml of DMF. The MOP-4 solution was kept for 1 day. Benzophenone (0.00164 g, 0.009 mmol) was dissolved in the MOP solution and 0.05 ml of diethyl ether and 0.05 ml of methanol were added to the MOP solution. The MOP solution was purged with Ar gas for 30 seconds. The solution placed with UV light at 365 nm and magnetic. After UV irradiation for 30 minutes, the solution was changed to clear with white precipitate from blue solution. After an additional hour of UV irradiation, a black precipitate was formed from a white precipitate. The blacker precipitate was formed with further UV irradiation.

**L1:** Owing to observe absorbance from 400 nm to 250 nm at UV-Vis spectra, the 0.05 mM solution was used **L1** (0.0033 g, 0.009 mmol) was dissolved in 3 ml DMF to make **L1** stock solution (3 mM). The 333  $\mu\text{l}$  stock solution was diluted with 667  $\mu\text{l}$  of DMF. 125  $\mu\text{l}$  of the diluted solution (1 mM) was diluted with 2.125 ml of DMF. The 125  $\mu\text{l}$  diethyl ether and 125  $\mu\text{l}$  methanol were added to the double diluted solution. This ligand solution was purged with Ar gas for 30 seconds. The solution placed with UV light at 365 nm while stirring.

**Benzophenone:** Owing to observe absorbance from 400 nm to 250 nm at UV-Vis spectra, the 0.05 mM solution was used benzophenone (0.0017 g, 0.009 mmol) was dissolved in 3 ml of DMF to make benzophenone stock solution (3 mM). The 333  $\mu\text{l}$  stock solution was diluted with 667  $\mu\text{l}$  of DMF. 125  $\mu\text{l}$  of the diluted solution (1 mM) was diluted with 2.125 ml of DMF. The 125

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$\mu$ l diethyl ether and 125  $\mu$ l methanol were added to the double diluted solution. This benzophenone solution was purged with Ar gas for 30 seconds. The solution placed with UV light at 365 nm while stirring.

**L1 and benzophenone:** Owing to observe absorbance from 400 nm to 250 nm at UV-Vis spectra, the 0.05 mM solution was used **L1** (0.0033 g, 0.009 mmol) was dissolved in 3 ml of DMF to make **L1** stock solution (3 mM) and benzophenone (0.0017 g, 0.009 mmol) was dissolved in 3 ml of DMF to make benzophenone stock solution (3 mM). The 333  $\mu$ l **L1** stock solution was diluted with 667  $\mu$ l of DMF and the 333  $\mu$ l benzophenone stock solution was diluted with 667  $\mu$ l of DMF. 125  $\mu$ l of the diluted **L1** solution (1 mM) and 125  $\mu$ l of the diluted benzophenone solution (1 mM) were mixed and then they were diluted with 2 ml of DMF. The 125  $\mu$ l diethyl ether and 125  $\mu$ l methanol were added to the double diluted solution. This mixed solution was purged with Ar gas for 30 seconds. The solution placed with UV light at 365 nm while stirring.

**MOP-1 and benzophenone:** Owing to observe absorbance from 400 nm to 250 nm at UV-Vis spectra, the 0.05 mM solution was obtained from coumarin-MOP-1 stock solution (3 mM against  $\text{Cu}^{2+}$ ) and benzophenone stock solution (3 mM). The 333  $\mu$ l coumarin-MOP-1 stock solution was diluted with 667  $\mu$ l of DMF and the 333  $\mu$ l benzophenone stock solution was diluted with 667  $\mu$ l of DMF. 125  $\mu$ l of the diluted coumarin-MOP-1 solution (1 mM) and 125  $\mu$ l of the diluted benzophenone solution (1 mM) were mixed and then they were diluted with 2 ml of DMF. The 125  $\mu$ l diethyl ether and 125  $\mu$ l methanol were added to the double diluted solution. This mixed solution was purged with Ar gas for 30 seconds. The solution placed with UV light at 365 nm while stirring.

### 6. Single Crystal X-ray Crystallography

A Coumarin-MOP-1 crystal was mounted onto a loop from mother liquid for single crystal X-ray data collection. Diffractions were measured on a Bruker Smart Apex diffractometer equipped with a Mo-K $\alpha$  sealed-tube X-ray source ( $\lambda = 0.71073 \text{ \AA}$ ) and liquid nitrogen stream (100 K). The data frames were recorded using APEX2 (v2012.2.0) and processed using the program *SAINT* (v7.68A) within APEX2. Absorption and beam corrections based on the multi-scan technique were applied to the integrated data using *SADABS* (v2008/1). All the structures were solved by direct method using *SHELXT* and refined by full-matrix least-squares on  $F^2$  using *SHELXL-2016* software.

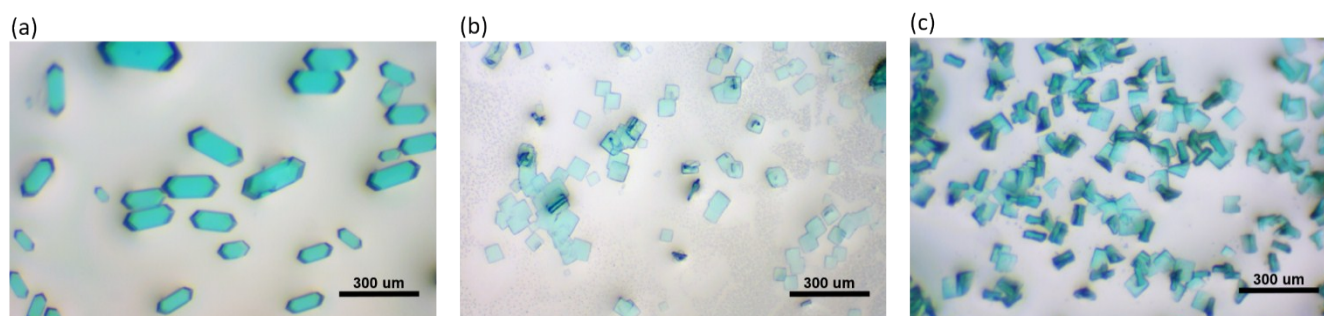
All non-hydrogen atoms needed to be refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were located in calculated positions with isotropic displacement parameters set to  $1.2 \times U_{\text{eq}}$  of the attached atoms. The solvent molecules were highly disordered, and attempts to locate and refine the solvent peaks were not always successful. Contributions to scattering due to these solvent molecules were removed using the *SQUEEZE* routine of *PLATON*; structures were then refined again using the data generated. . The refinement details and validation reply can be found in Supporting Information (section 2.1). The CIF file can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). CCDC numbers and the crystal information are listed in Table 1.

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**Table S1.** Crystal data and structure refinement for data.

Identification code (CCDC numbers)	Coumarin-MOP-1 (CCDC 1533032)
Empirical formula	$C_{496}H_{376}Cu_{24}N_8O_{224}$
Formula weight	11556.99
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	I 4/m
Unit cell dimensions	a = 35.309(3) Å $\alpha = 90^\circ$ b = 35.309(3) Å $\beta = 90^\circ$ c = 43.609(4) Å $\gamma = 90^\circ$
Volume	54368(10) Å <sup>3</sup>
Z	2
Density (calculated)	0.706 Mg/m <sup>3</sup>
Absorption coefficient	0.507 mm <sup>-1</sup>
F(000)	11792
Crystal size	0.200 x 0.180 x 0.170 mm <sup>3</sup>
Theta range for data collection	1.631 to 24.998°.
Index ranges	-41 ≤ h ≤ 41, -41 ≤ k ≤ 41, -51 ≤ l ≤ 51
Reflections collected	264858
Independent reflections	24245 [R(int) = 0.1085]
Completeness to theta = 24.998°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6783
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	24245 / 408 / 830
Goodness-of-fit on F <sup>2</sup>	1.111
Final R indices [I > 2σ(I)]	R1 = 0.0674, wR2 = 0.1714
R indices (all data)	R1 = 0.1418, wR2 = 0.2527
Largest diff. peak and hole	1.346 and -0.716 e.Å <sup>-3</sup>

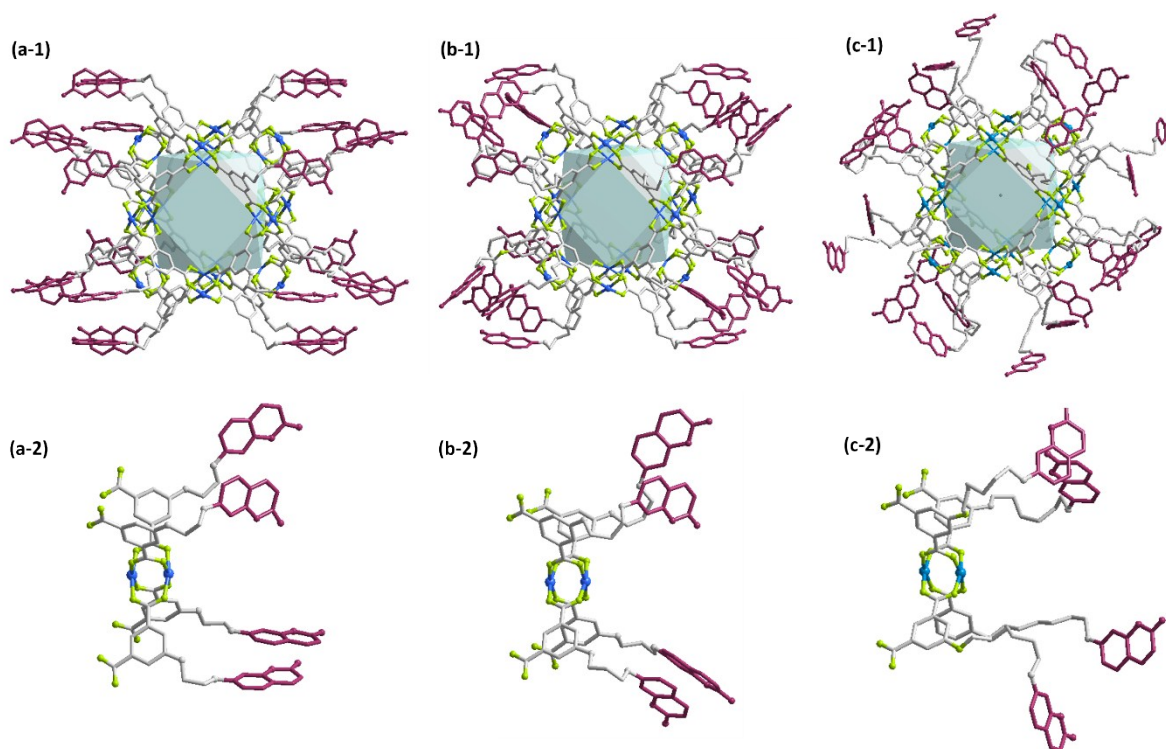
## SUPPORTING INFORMATION



**Figure S4.** Photographs from microscope of Coumarin-MOP-1 (a), Coumarin-MOP-2 (b), and Coumarin-MOP-3 (c).

### Part S3. Coumarin-MOP structures

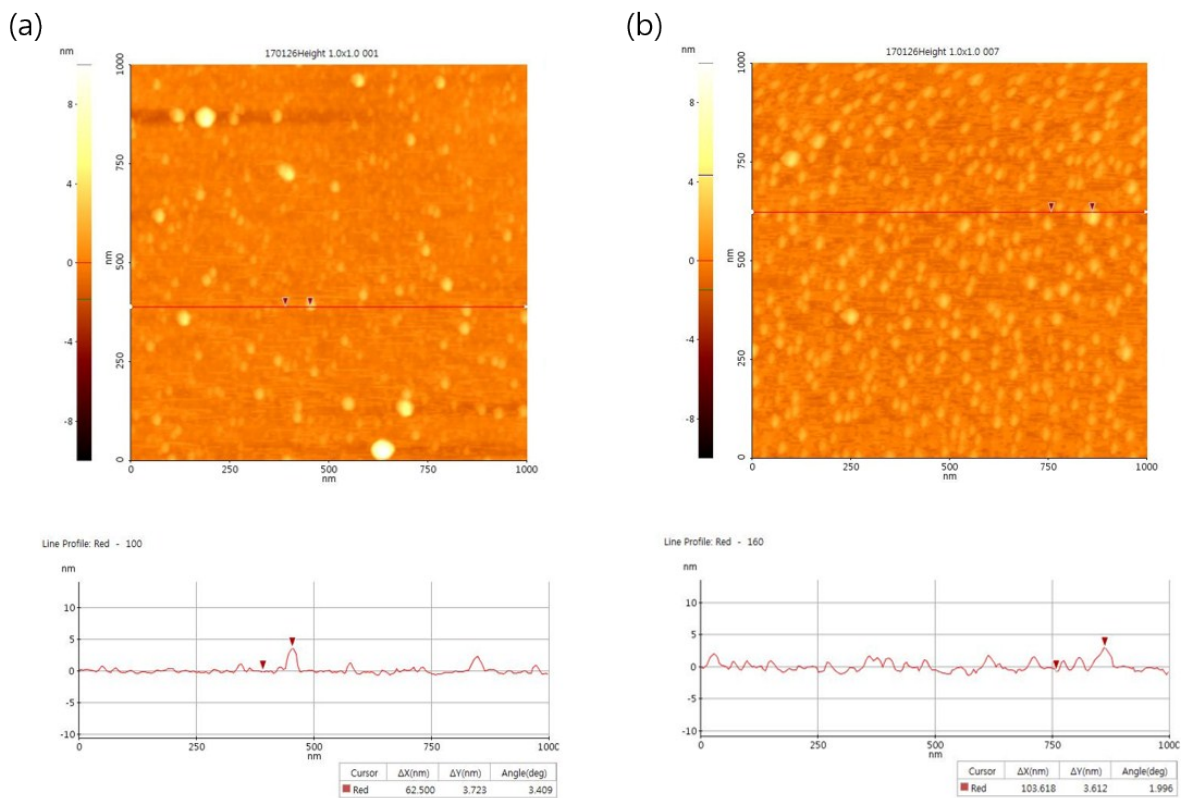
#### 1. Crystal or Simulated Coumarin-MOP structures



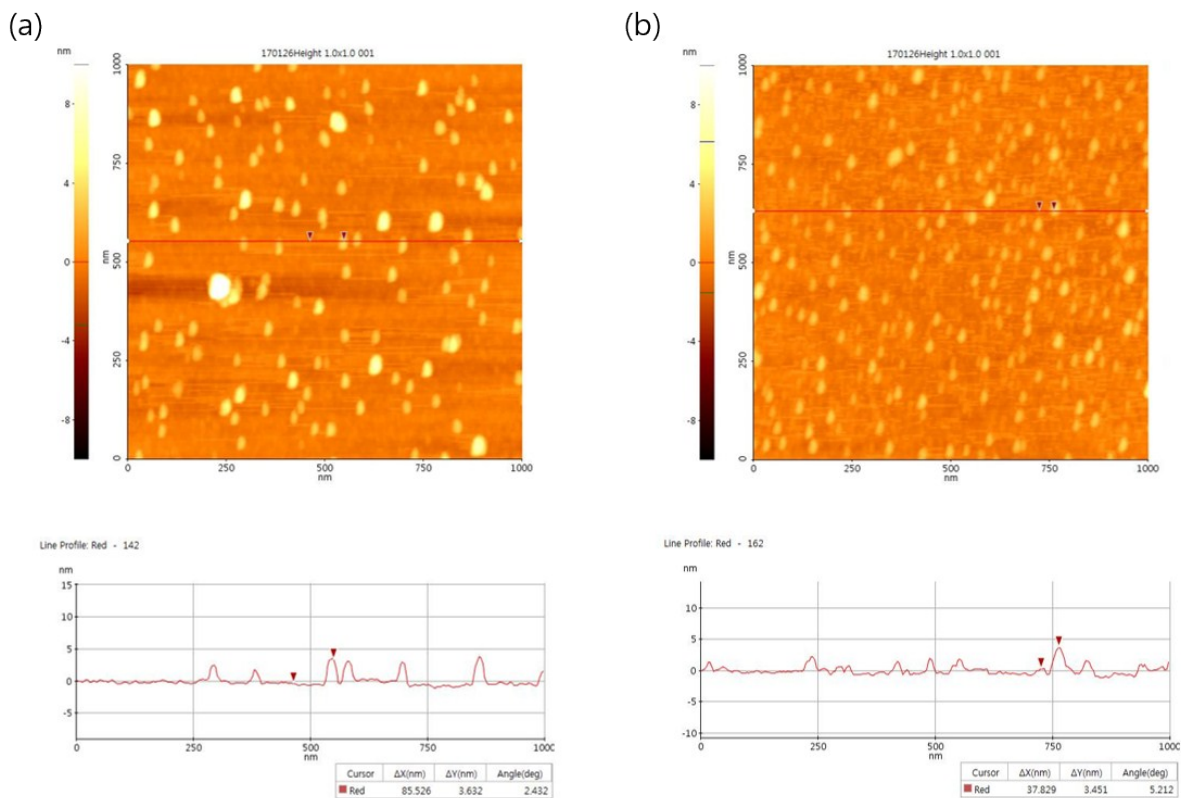
**Figure S5.** Structures of Coumarin-MOP-1 (a-1), Coumarin-MOP-2 (b-1), Coumarin-MOP-3 (c-1) and enlarged Cu-paddlewheel structures with four **L1** (a-2), **L2** (b-2), and **L3** (c-2). The structures of Coumarin-MOP-2 and Coumarin-MOP-3 were simulated using Forcite in Materials Studio.

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## 2. Atomic Force Microscopy (AFM) images

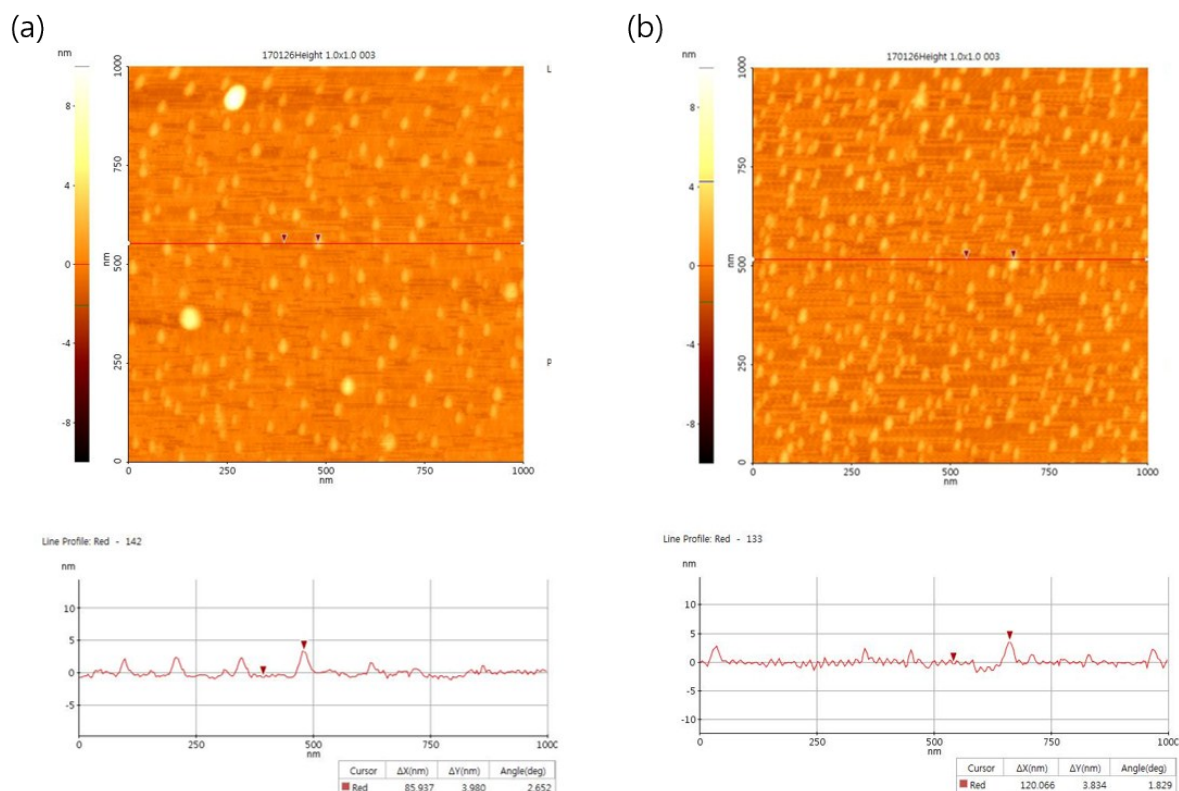


**Figure S6.** AFM images of Coumarin-MOP-1 before (a) and after (b) reduction to  $\text{Cu}^+$  state.



**Figure S7.** AFM images of Coumarin-MOP-2 before (a) and after (b) reduction to  $\text{Cu}^+$  state.

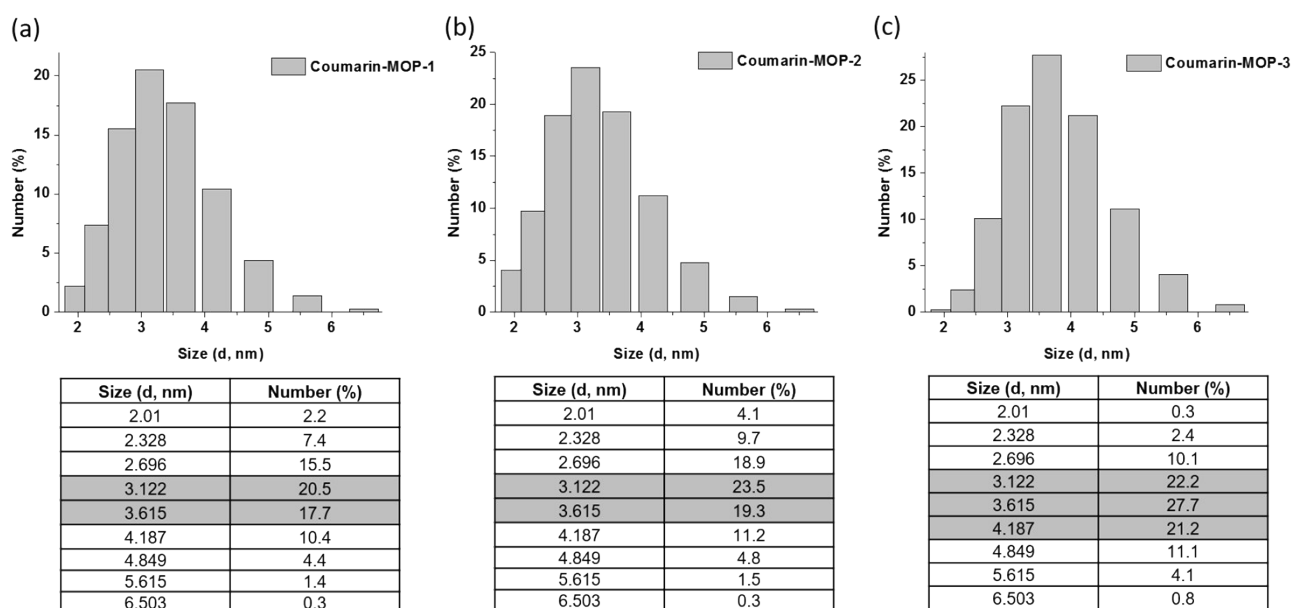
# SUPPORTING INFORMATION



**Figure S8.** AFM images of Coumarin-MOP-3 before (a) and after (b) reduction to  $\text{Cu}^+$  state.

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### 3. Dynamic Light Scattering (DLS) data



**Figure S9.** DLS measurement results of Coumarin-MOP-1 (a), Coumarin-MOP-2 (b), and Coumarin-MOP-3 (c).

### 4. Calculated and measured size of Coumarin-MOPs

**Table S2.** Calculated and measured size of Coumarin-MOPs.

	Crystal structure/ simulated structures (nm)	DLS (nm)	AFM (nm)
Coumarin-MOP-1	4.4	3.1-3.6	3.7-3.6
Coumarin-MOP-2	4.5	3.1-3.6	3.4-3.6
Coumarin-MOP-3	5.1	3.1-4.2	3.9-3.8

Part S4. UV-Vis spectra and Photographs

1. UV-Vis spectra of ligands

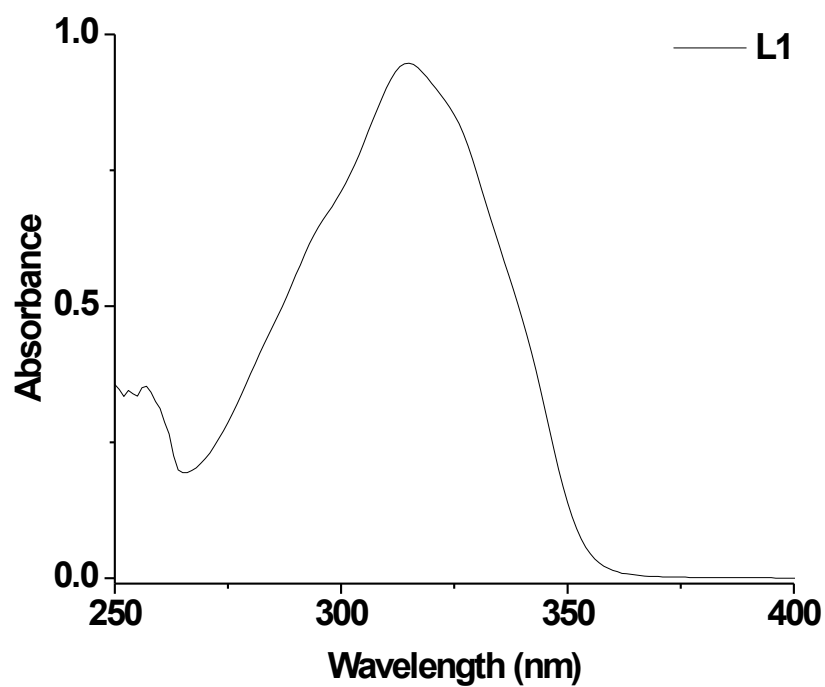


Figure S10. UV-Vis absorption spectrum of L1.

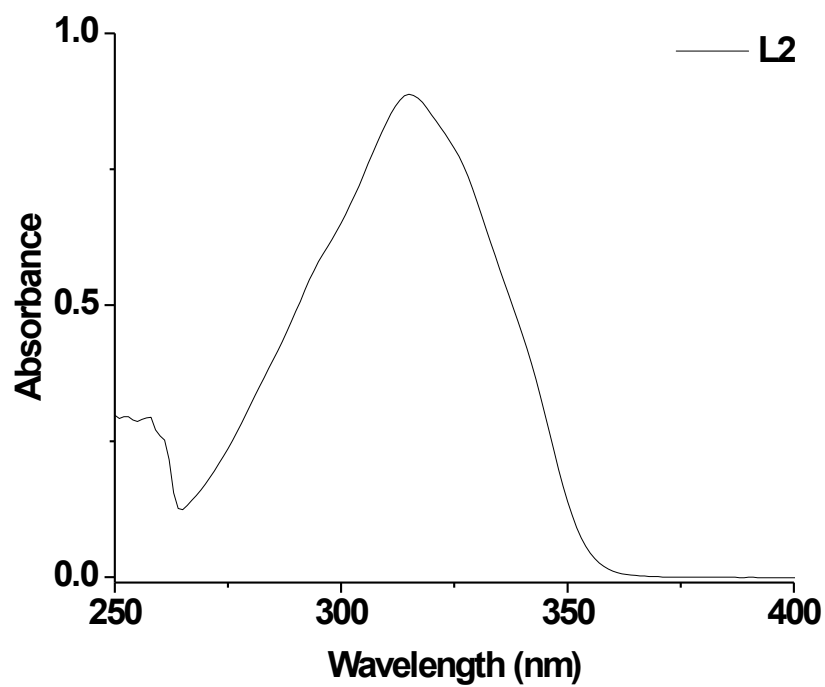


Figure S11. UV-Vis absorption spectrum of L2.



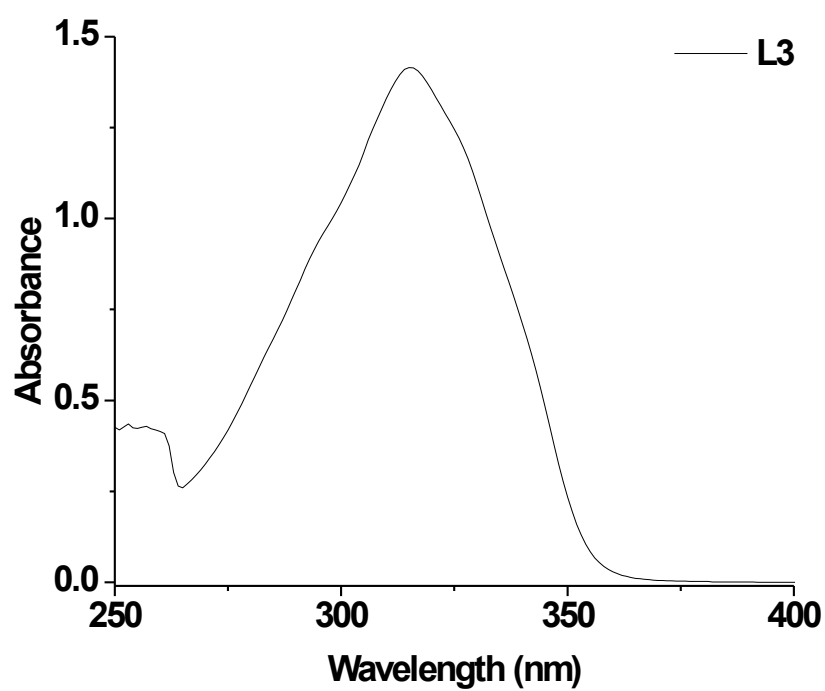


Figure S12. UV-Vis absorption spectrum of L3.

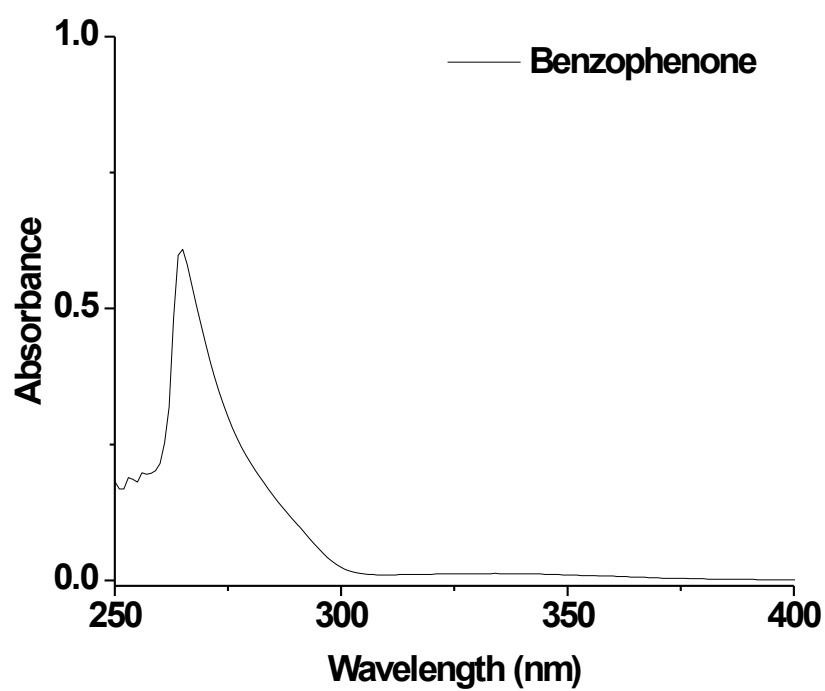


Figure S13. UV-Vis absorption spectrum of benzophenone.

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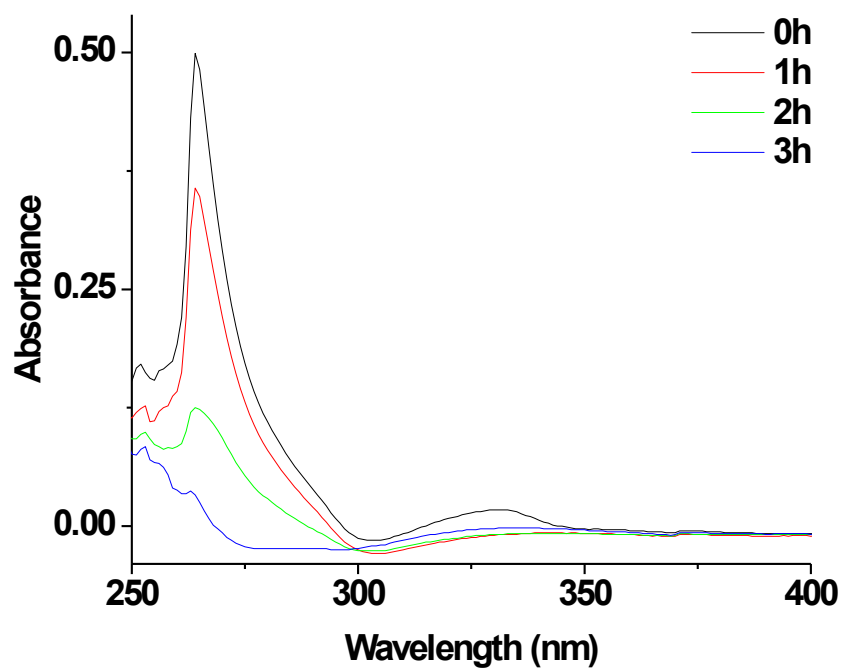


Figure S14. UV-Vis absorption spectra of benzophenone after every 1 h UV irradiation.

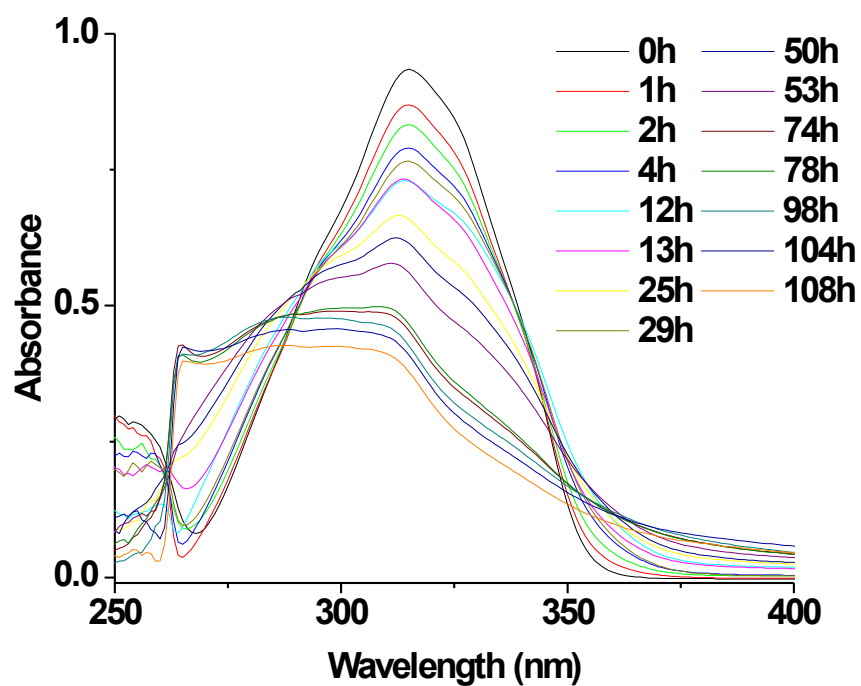


Figure S15. UV-Vis absorption spectra of L1 upon UV irradiation.

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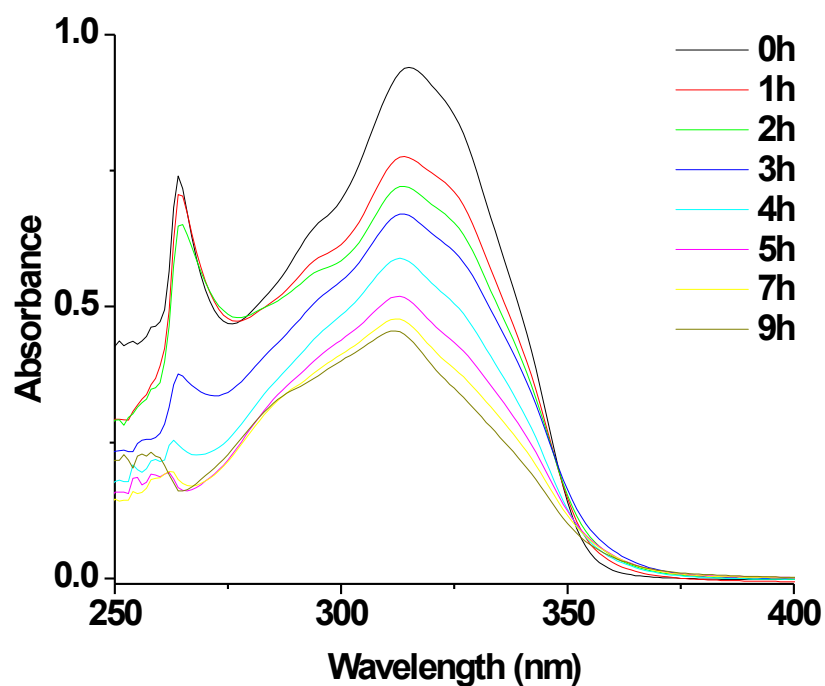


Figure S16. UV-Vis absorption spectra of L1 and benzophenone upon UV irradiation.

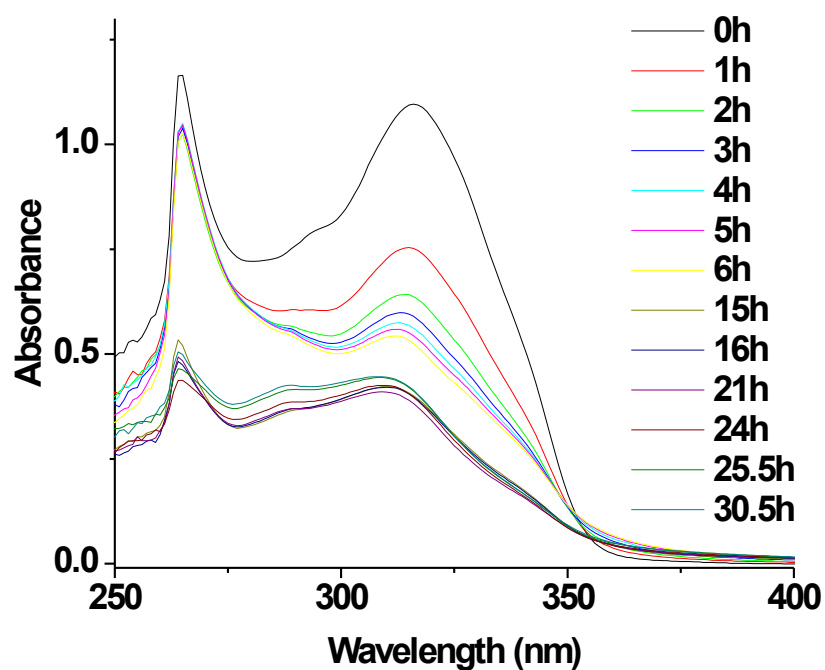
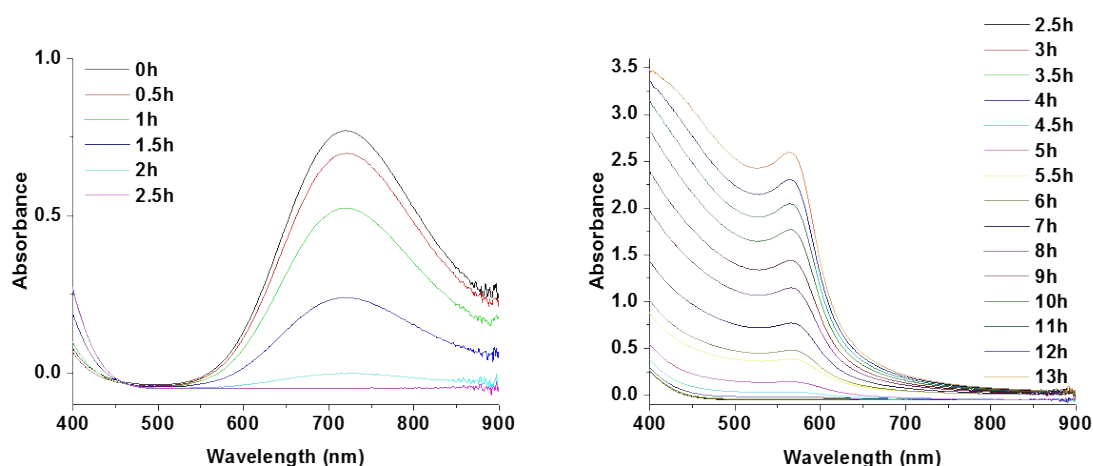


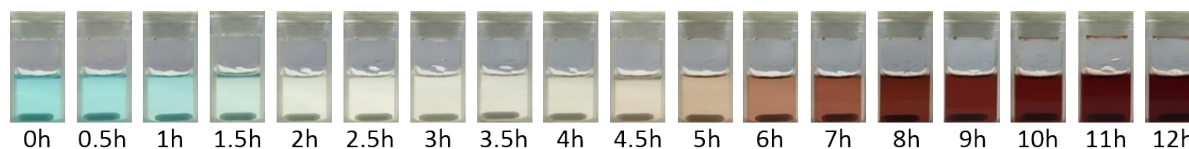
Figure S17. UV-Vis absorption spectra of Coumarin-MOP-1 and benzophenone upon UV irradiation.

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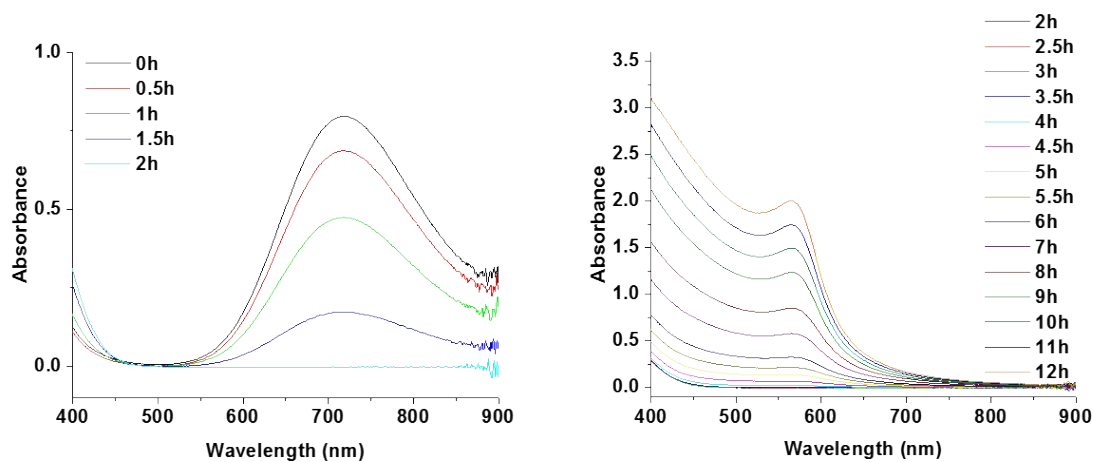
### 2. UV-Vis spectra and photographs of Coumarin-MOPs



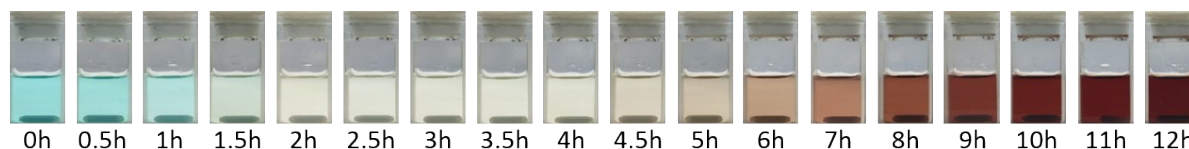
**Figure S18.** UV-Vis absorption spectra of Coumarin-MOP-1 and benzophenone upon UV irradiation.



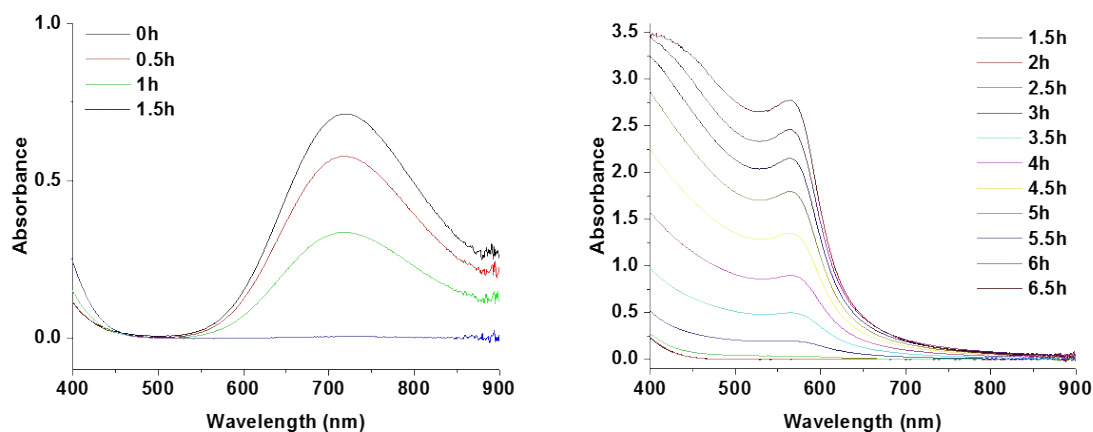
**Figure S19.** Photographs of Coumarin-MOP-1 during the  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  photoinduced reduction process. The hours indicate the UV irradiation time.



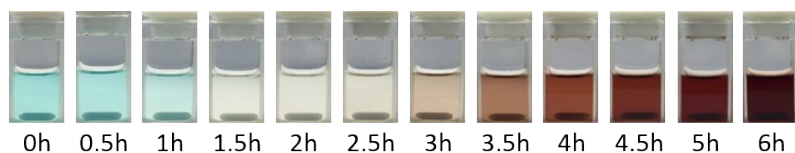
**Figure S20.** UV-Vis absorption spectra of Coumarin-MOP-2 and benzophenone upon UV irradiation.



**Figure S21.** Photographs of Coumarin-MOP-2 during the  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  photoinduced reduction process. The hours indicate the UV irradiation time.

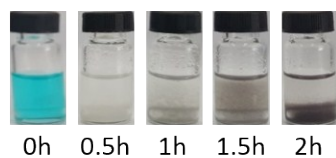


**Figure S22.** UV-Vis absorption spectra of Coumarin-MOP-3 and benzophenone upon UV irradiation.

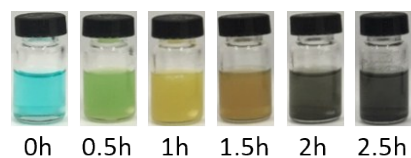


**Figure S23.** Photographs of Coumarin-MOP-3 during the  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  photoinduced reduction process. The hours indicate the UV irradiation time.

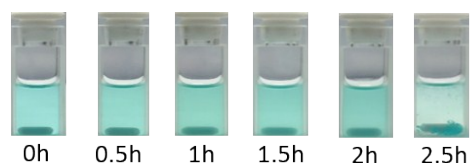
### 3. UV-Vis spectra and photographs for the control experiments



**Figure S24.** Photographs of MOP-4 during the  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  photoinduced reduction process. The hours indicate the UV irradiation time.

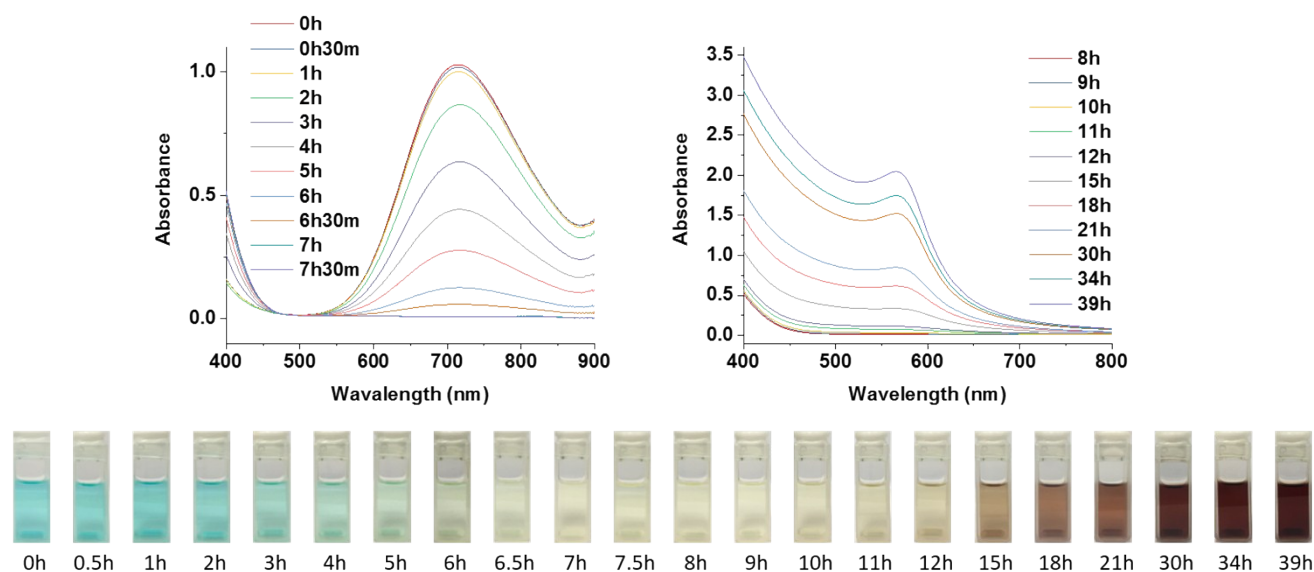


**Figure S25.** Photographs of  $\text{Cu}(\text{CH}_3\text{COO})_2$  during the  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  photoinduced reduction process. The hours indicate the UV irradiation time.

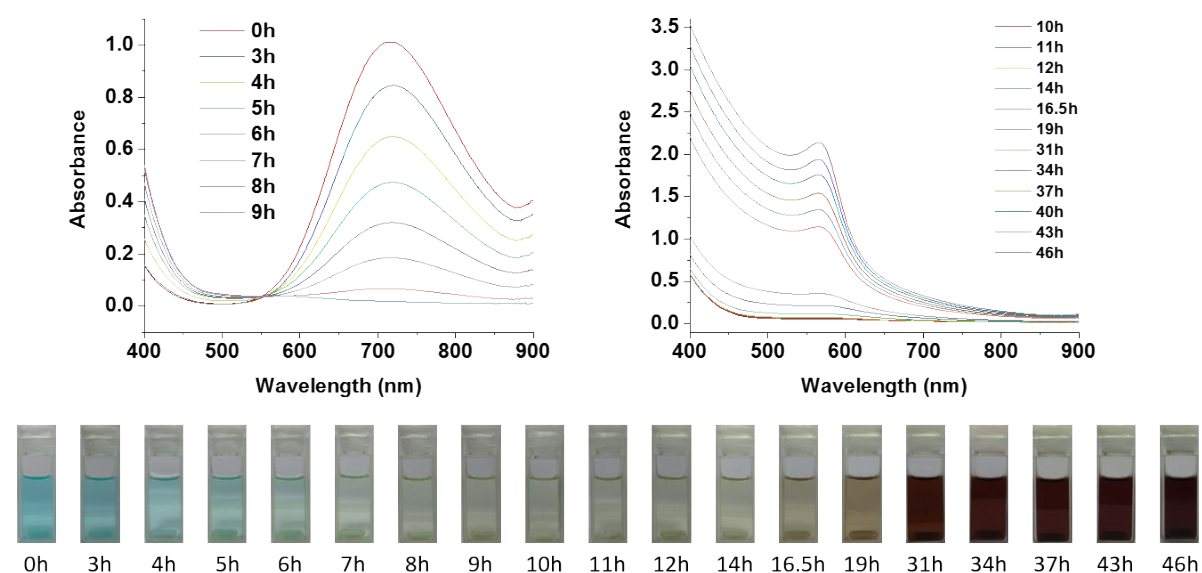


**Figure S26.** Photographs of MOP-4 with Coumarin during the  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  photoinduced reduction process. The hours indicate the UV irradiation time.

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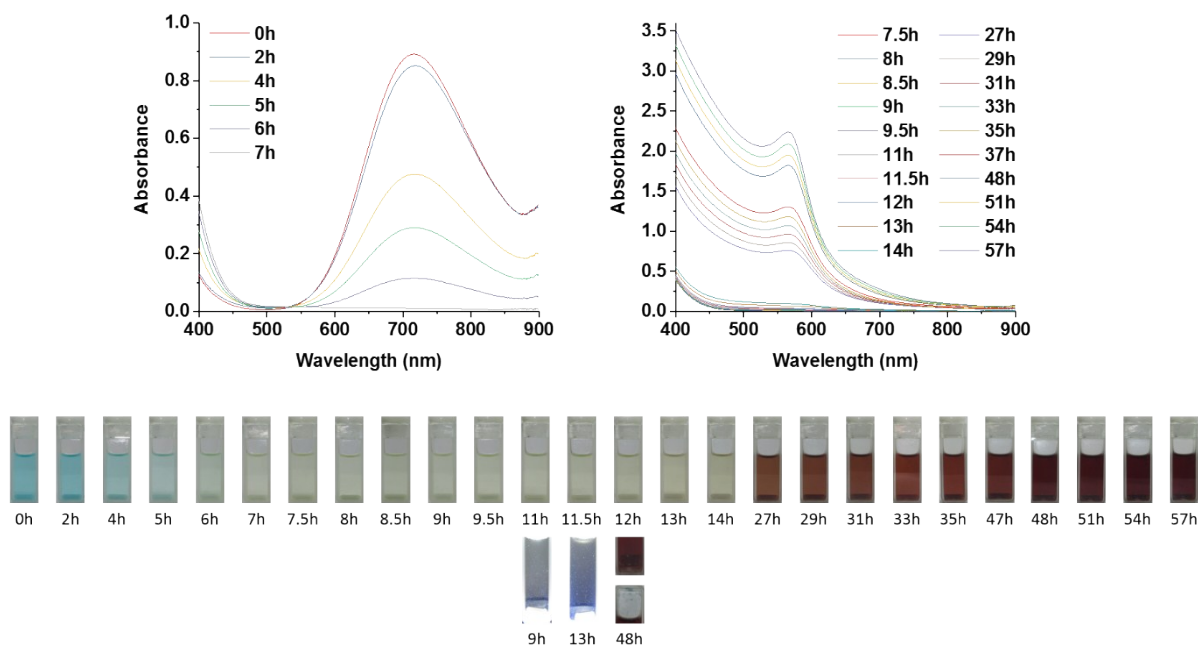


**Figure S27.**  $\text{Cu}^{2+}$  reduction with the use of one quarter equivalent benzophenone against  $\text{Cu}^{2+}$ .



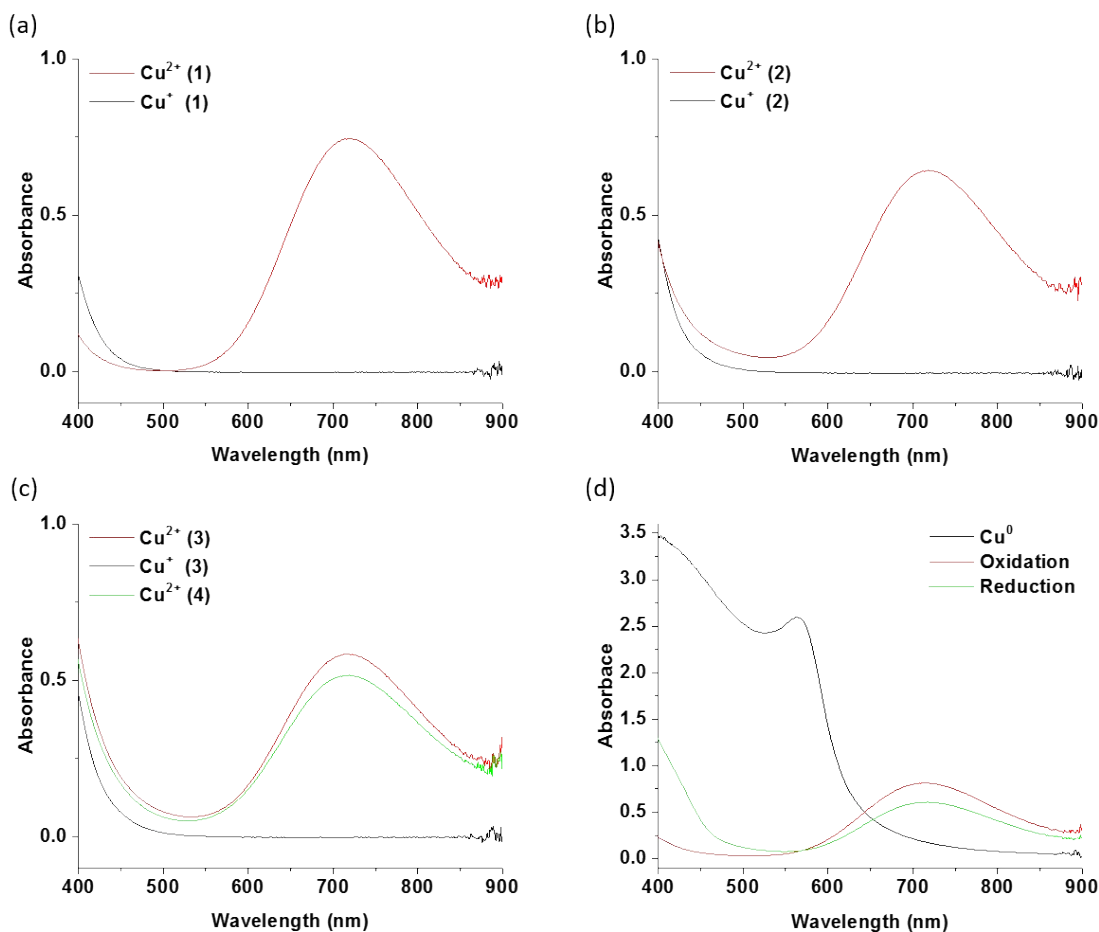
**Figure S28.**  $\text{Cu}^{2+}$  reduction in the absence of methanol in the solvents.

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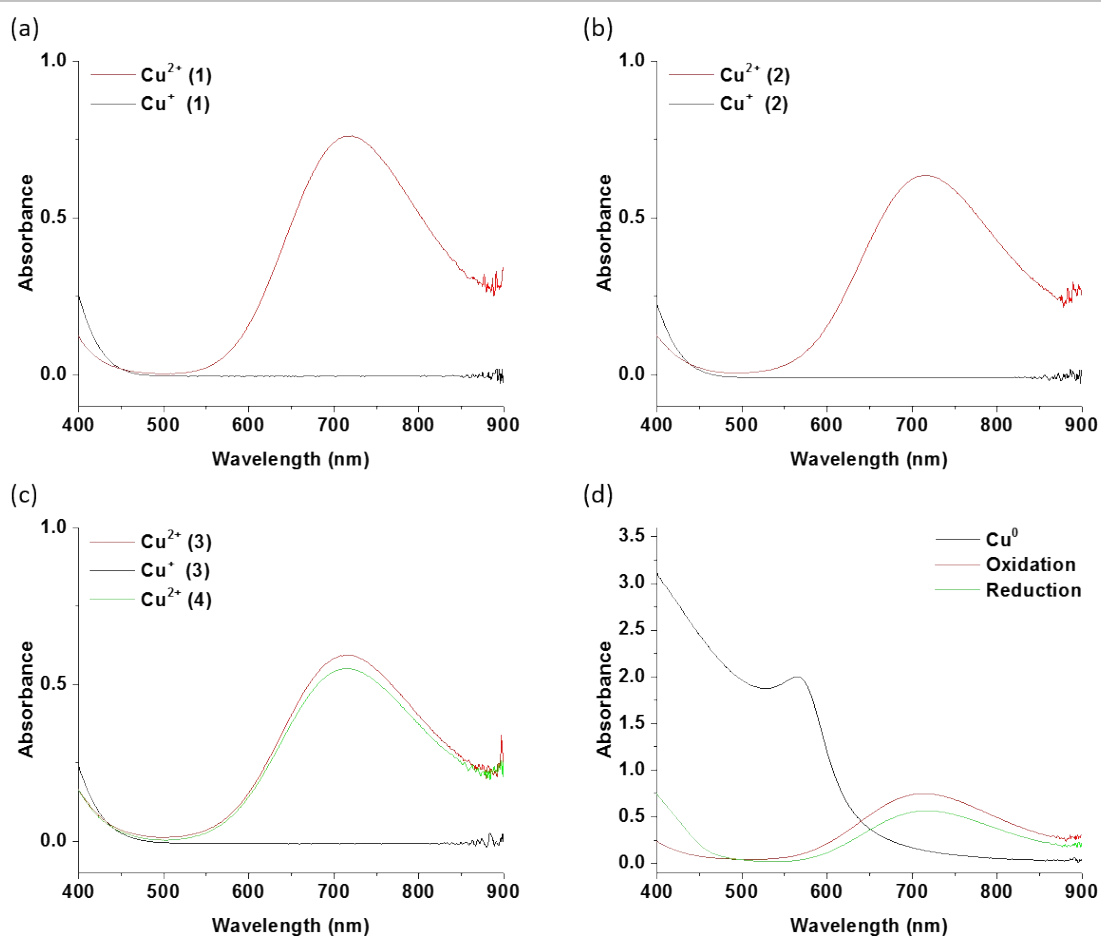
**Figure S29.**  $\text{Cu}^{2+}$  reduction in the absence of ethers in the solvents.

### 4. UV-Vis spectra for the reversible reduction experiments



**Figure S30.** UV-Vis absorption spectra of Coumarin-MOP-1 for (a) the first, (b) second, and (c) third cycles of the reversibility test. (d) UV-Vis absorption spectra after  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  reduction, oxidation, and the second reduction of Coumarin-MOP-1.

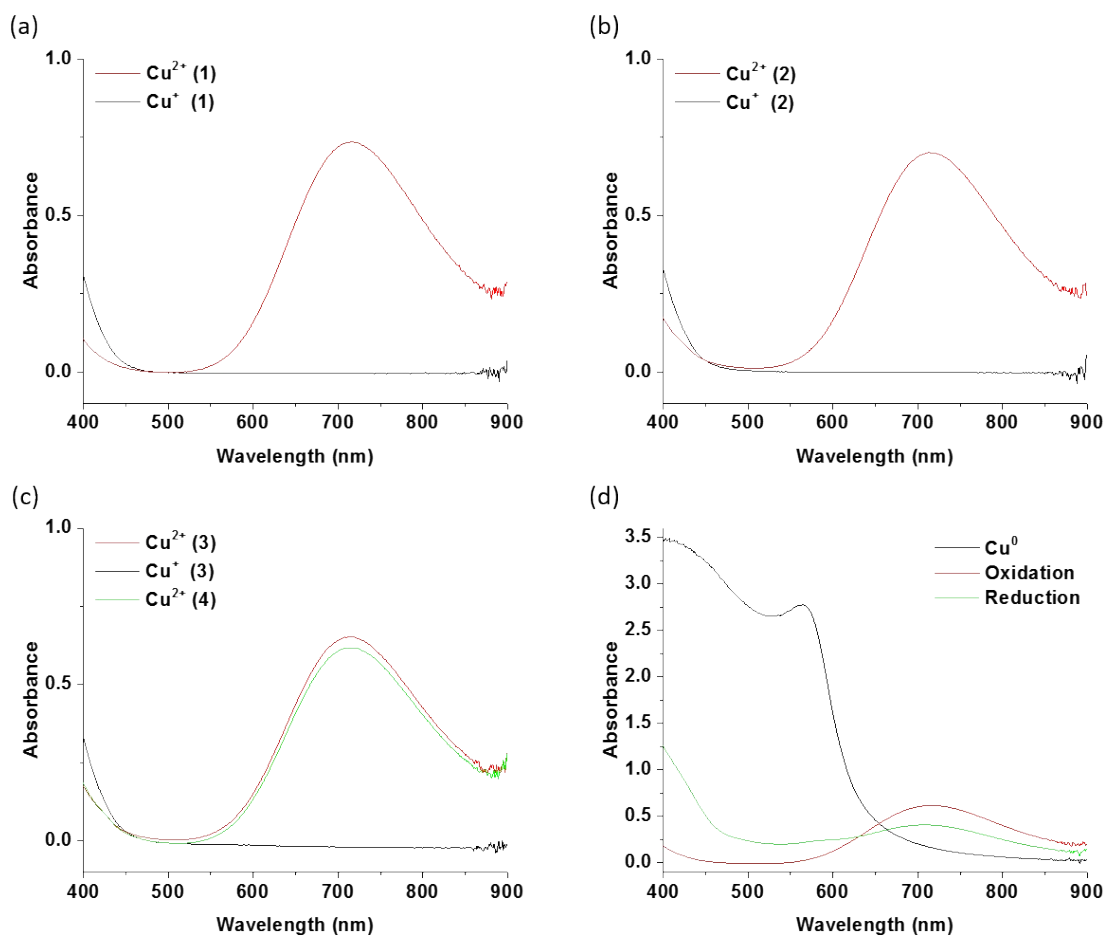
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**Figure S31.** UV-Vis absorption spectra of Coumarin-MOP-2 for (a) the first, (b) second, and (c) third cycles of the reversibility test. (d) UV-Vis absorption spectra after  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  reduction, oxidation, and the second reduction of Coumarin-MOP-2.

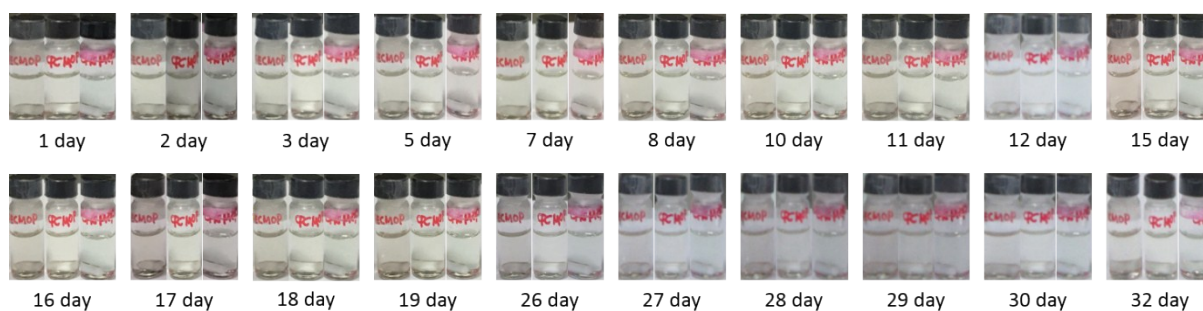


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**Figure S32.** UV-Vis absorption spectra of Coumarin-MOP-3 for (a) the first, (b) second, and (c) third cycles of the reversibility test. (d) UV-Vis absorption spectra after  $\text{Cu}^{2+}$  to  $\text{Cu}^0$  reduction, oxidation, and the second reduction of Coumarin-MOP-3.

### 5. Stability test of the $\text{Cu}^+$ state



**Figure S33.** Stability test of the  $\text{Cu}^+$  state.

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### Part S5. Additional Characterization

#### 1. Fourier transform nuclear magnetic resonance spectrometer (NMR) Data

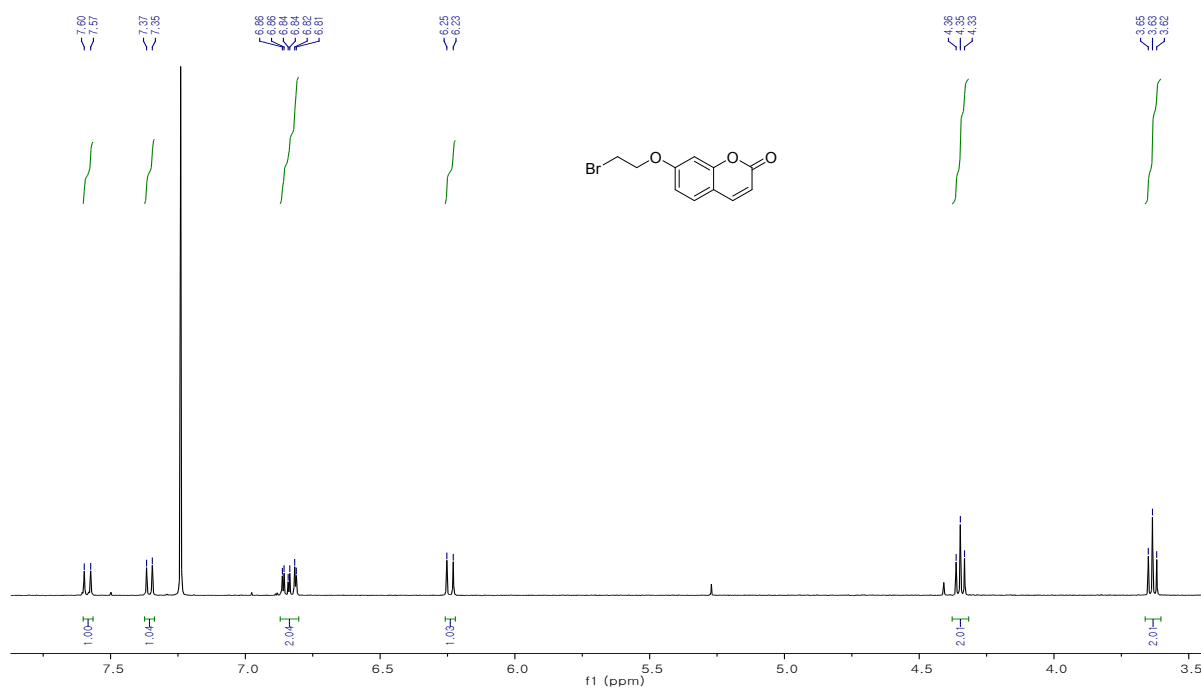


Figure S34. <sup>1</sup>H-NMR spectrum of L1-(a).

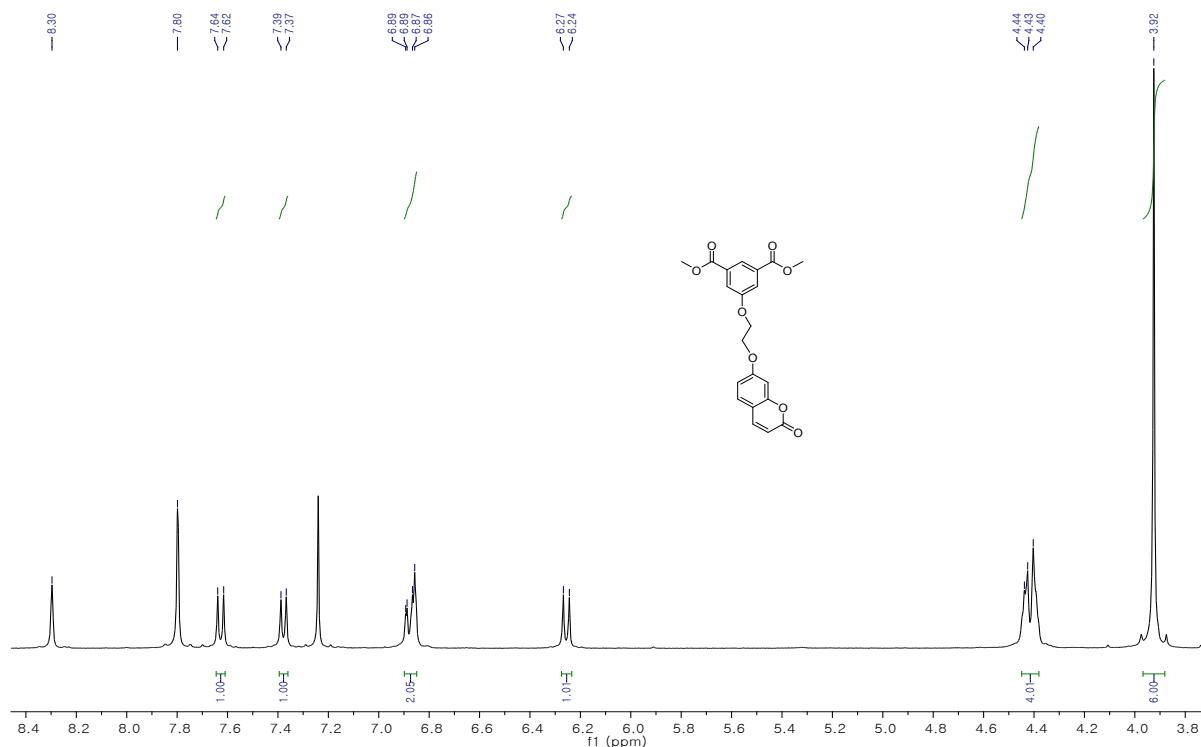


Figure S35. <sup>1</sup>H-NMR spectrum of L1-(b).

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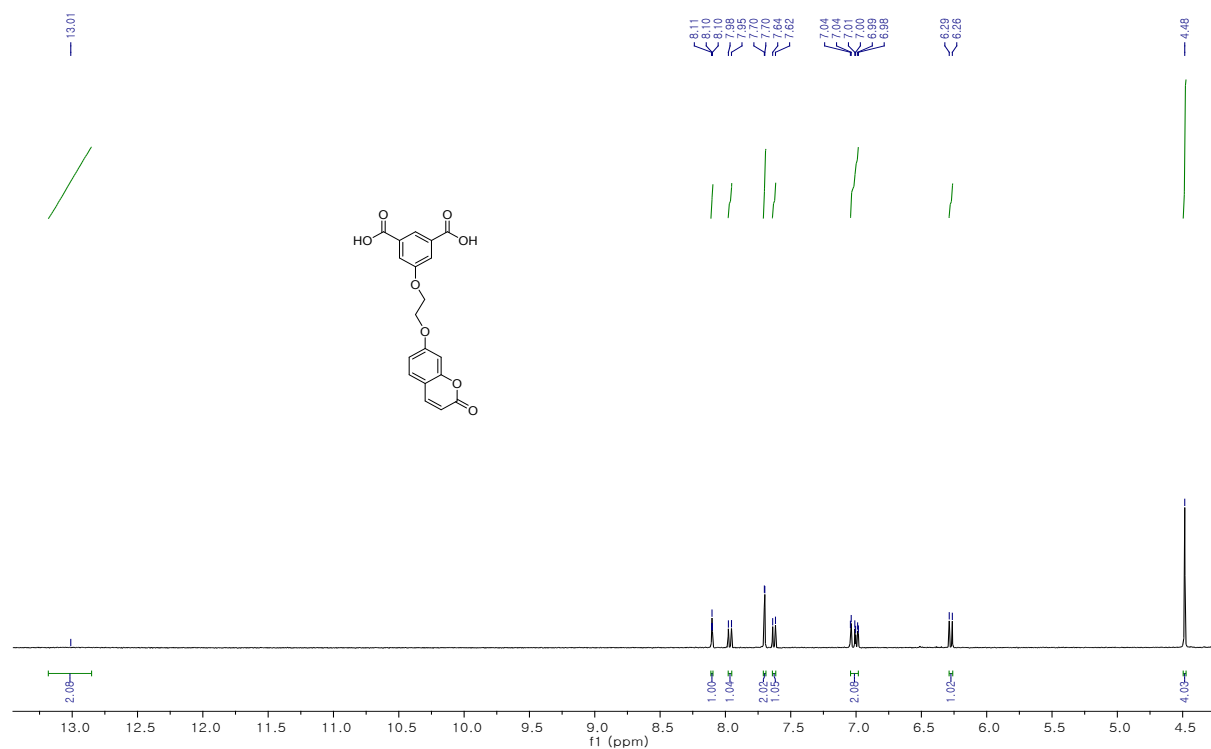


Figure S36. <sup>1</sup>H-NMR spectrum of (c) of L1-(c).

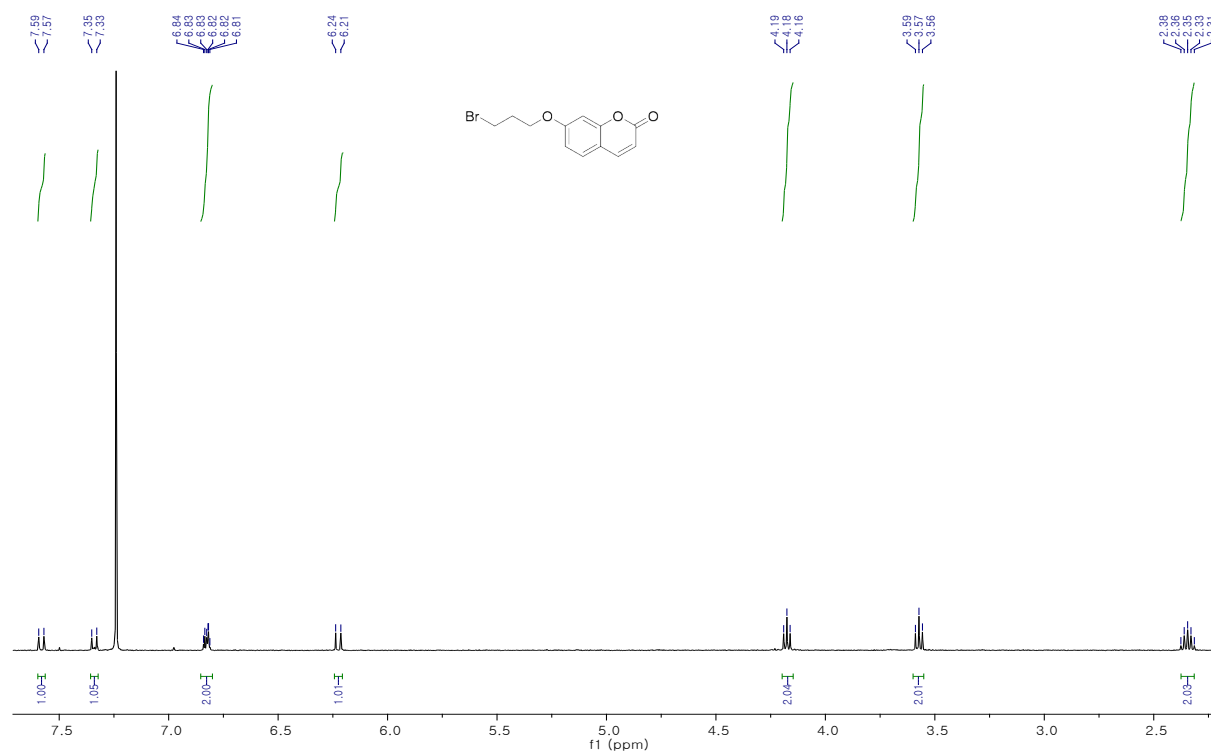
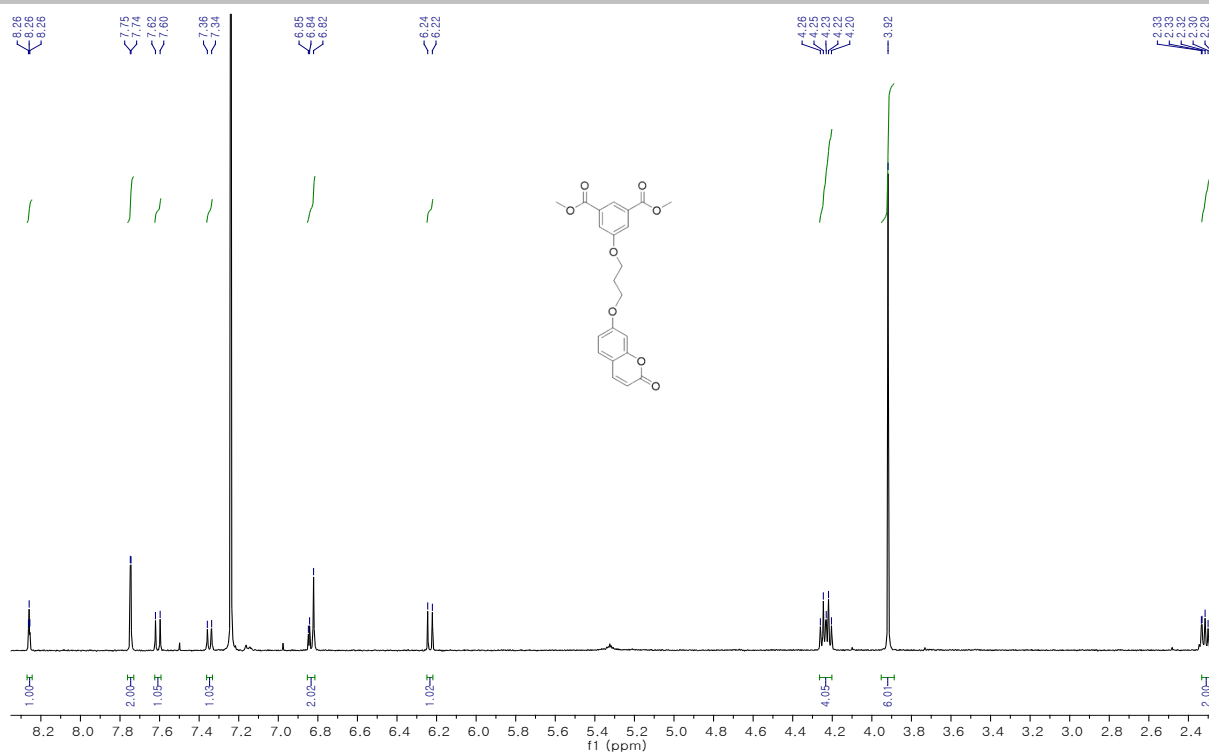
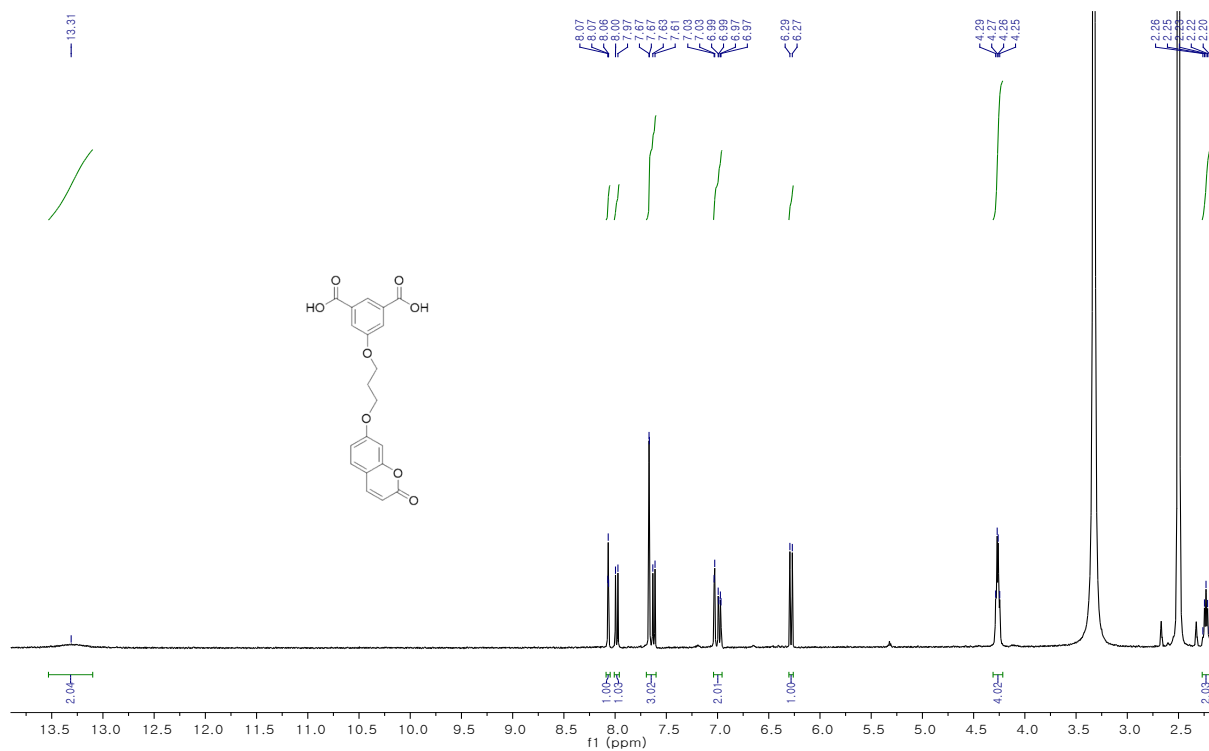


Figure S37. <sup>1</sup>H-NMR spectrum of L2-(d).

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**Figure S38. <sup>1</sup>H-NMR spectrum of L2-(e).**



**Figure S39. <sup>1</sup>H-NMR spectrum of L2-(f).**

# SUPPORTING INFORMATION

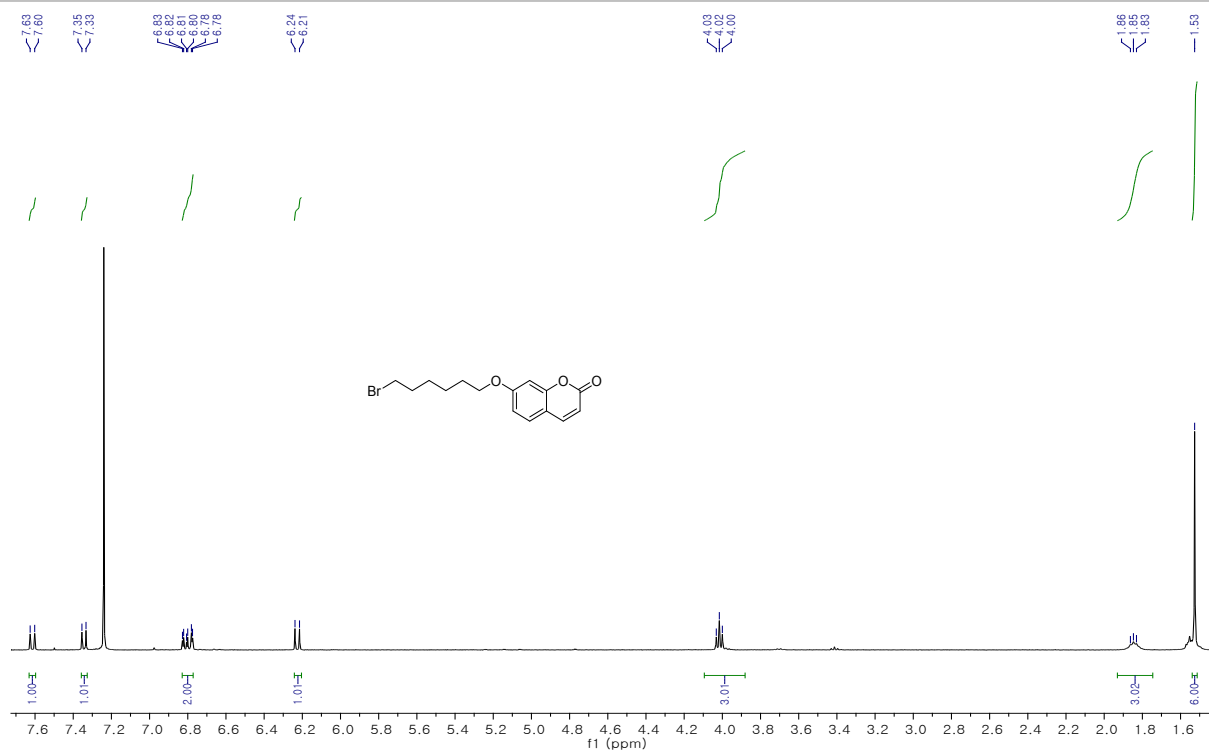


Figure S40. <sup>1</sup>H-NMR spectrum of L3-(g).

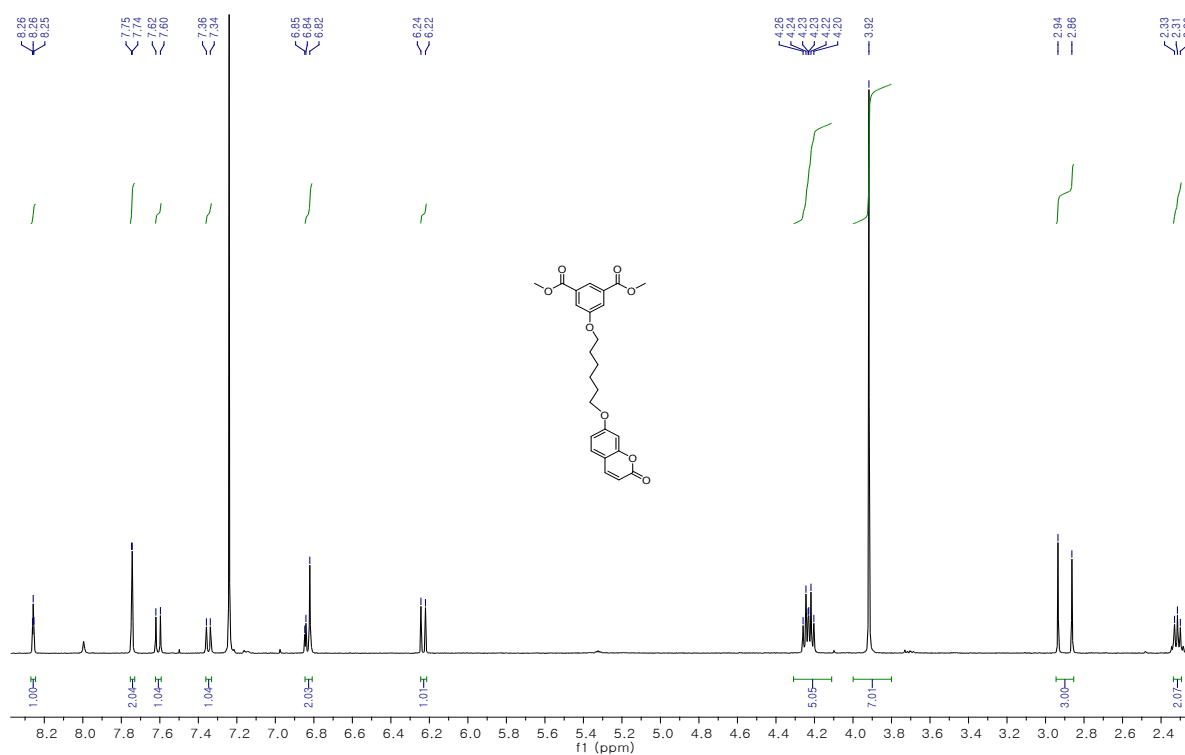
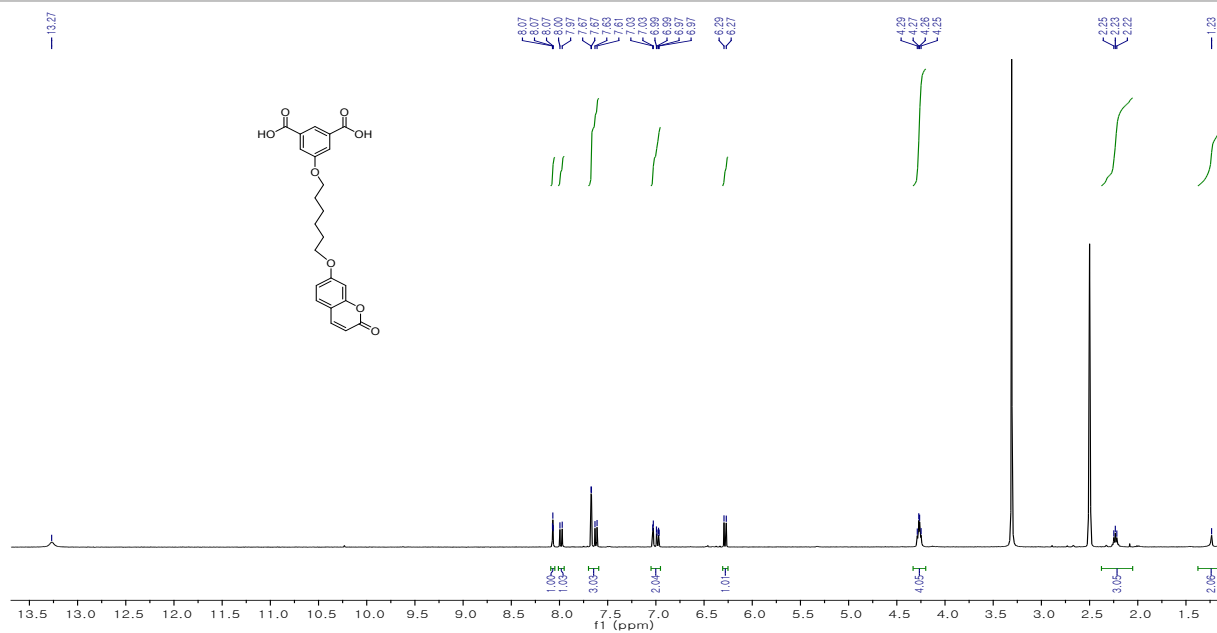
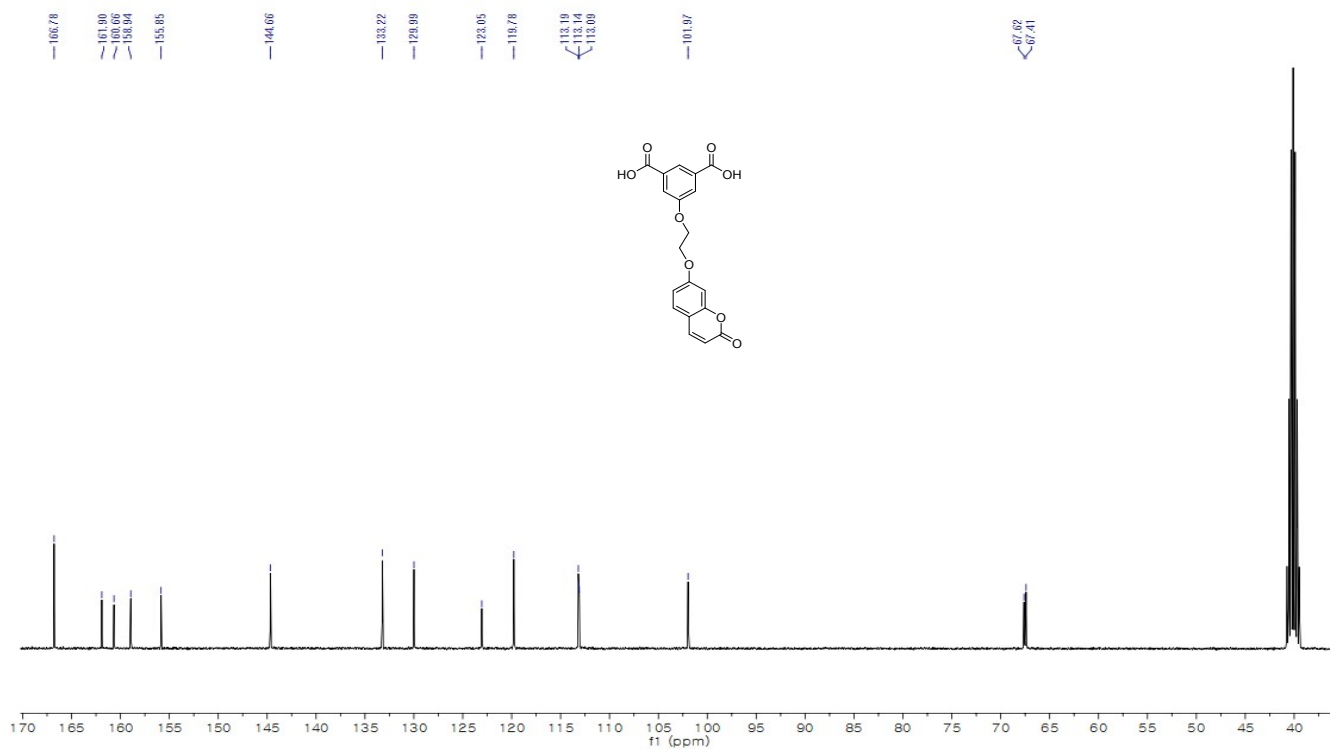


Figure S41. <sup>1</sup>H-NMR spectrum of L3-(h).

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**Figure S42.** <sup>1</sup>H-NMR spectrum of L3-(i).



**Figure S43.** <sup>13</sup>C-NMR spectrum of L1-(c).

# SUPPORTING INFORMATION

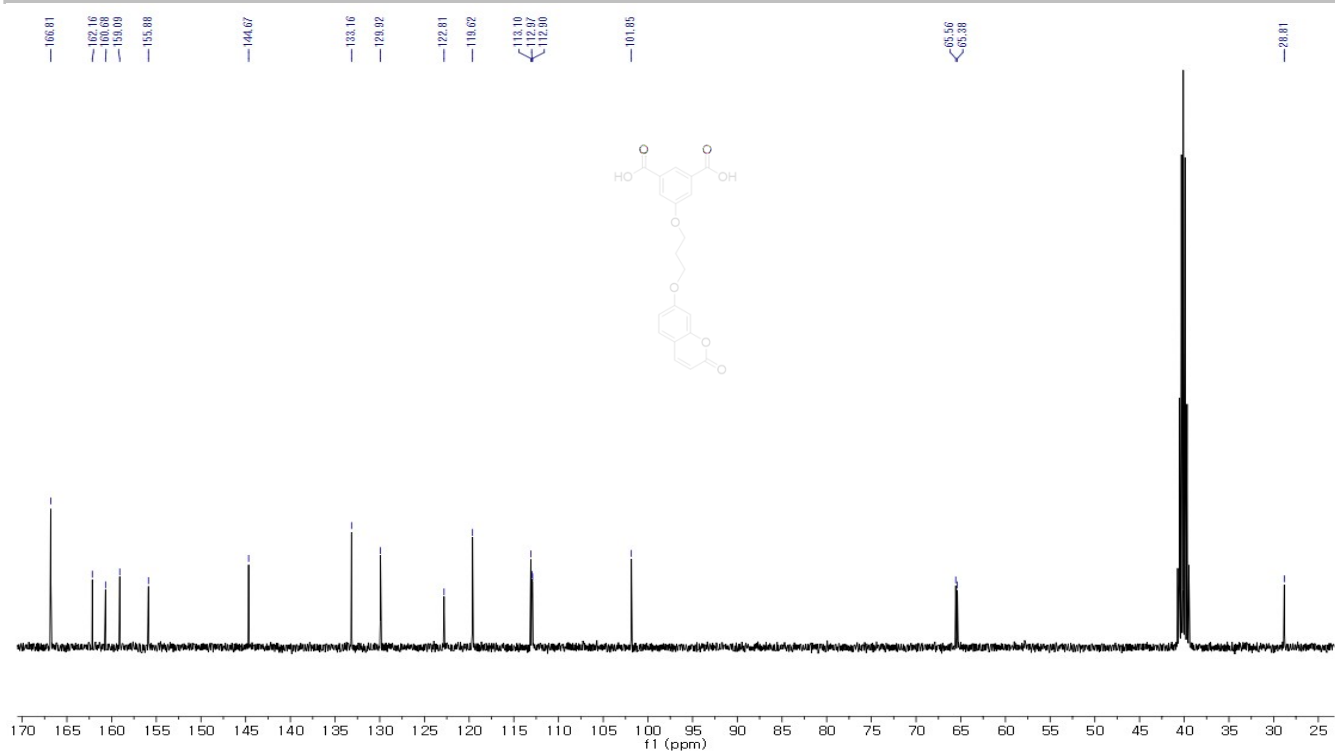


Figure S44. <sup>13</sup>C-NMR spectrum of L2-(f).

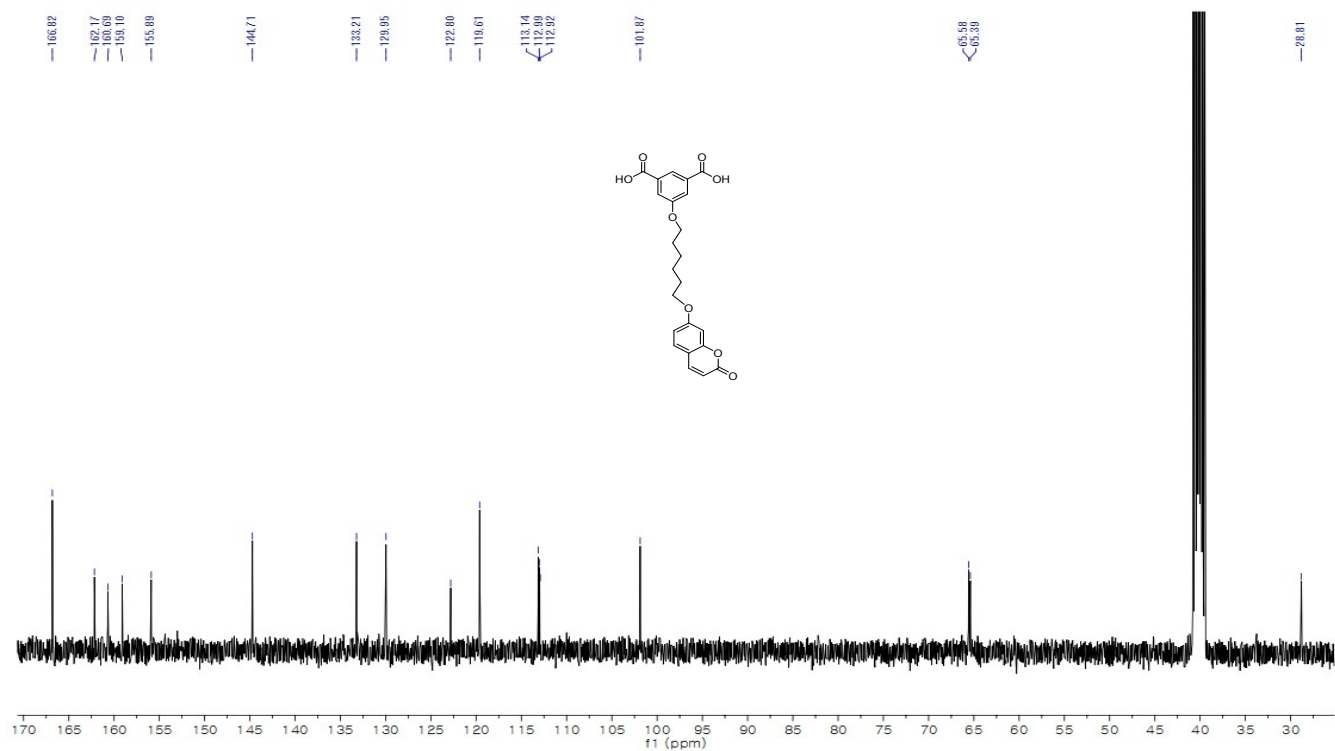


Figure S45. <sup>13</sup>C-NMR spectrum of L3-(i).

## SUPPORTING INFORMATION

### 2. Fourier transform nuclear magnetic resonance spectrometer (FT-IR) Data

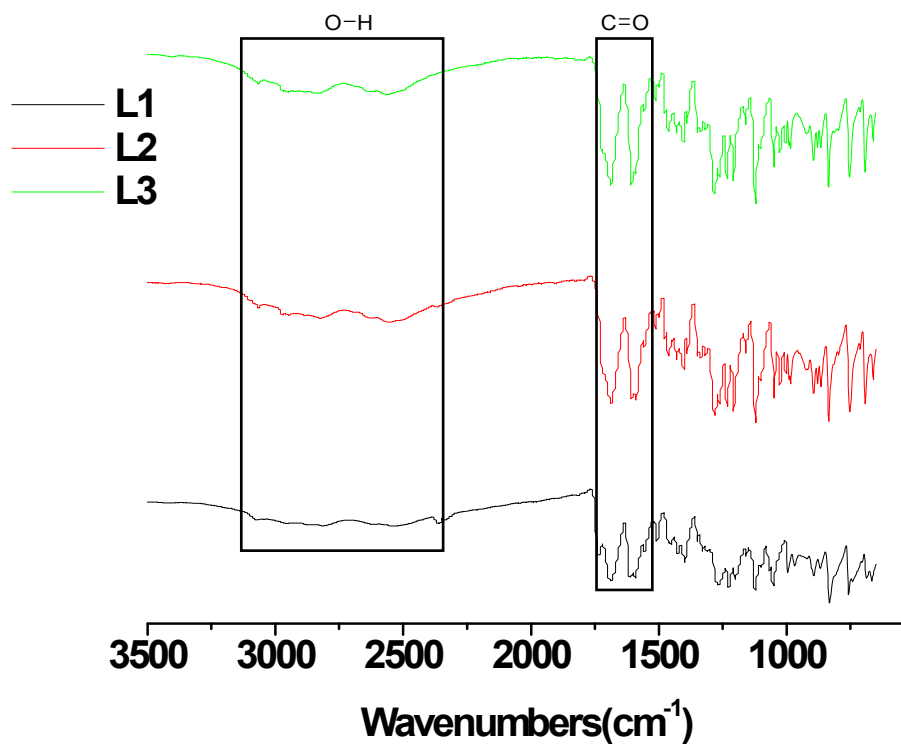


Figure S46. FT-IR spectra of L1, L2, and L3.

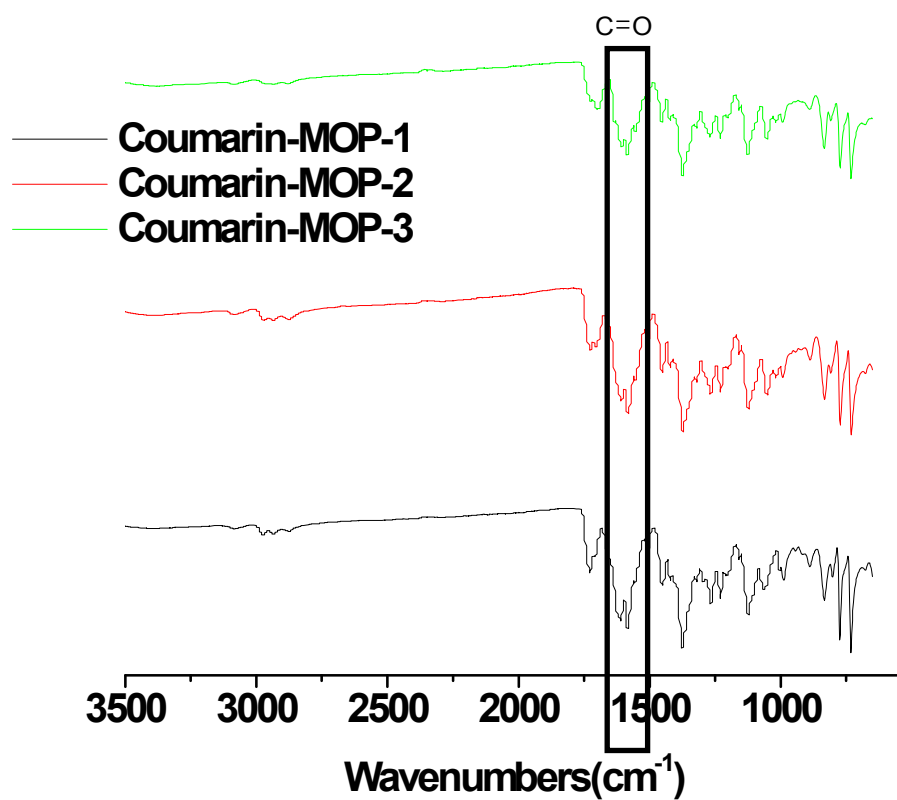


Figure S47. FT-IR spectra of Coumarin-MOP-1, -2, and -3.



## SUPPORTING INFORMATION

### 3. Thermogravimetric analyzer (TGA) Data

**Sample preparation:** For TGA analysis, the crystalline precipitates of coumarin-MOPs were washed with diethylethers for three times and then dried at RT under vacuum.

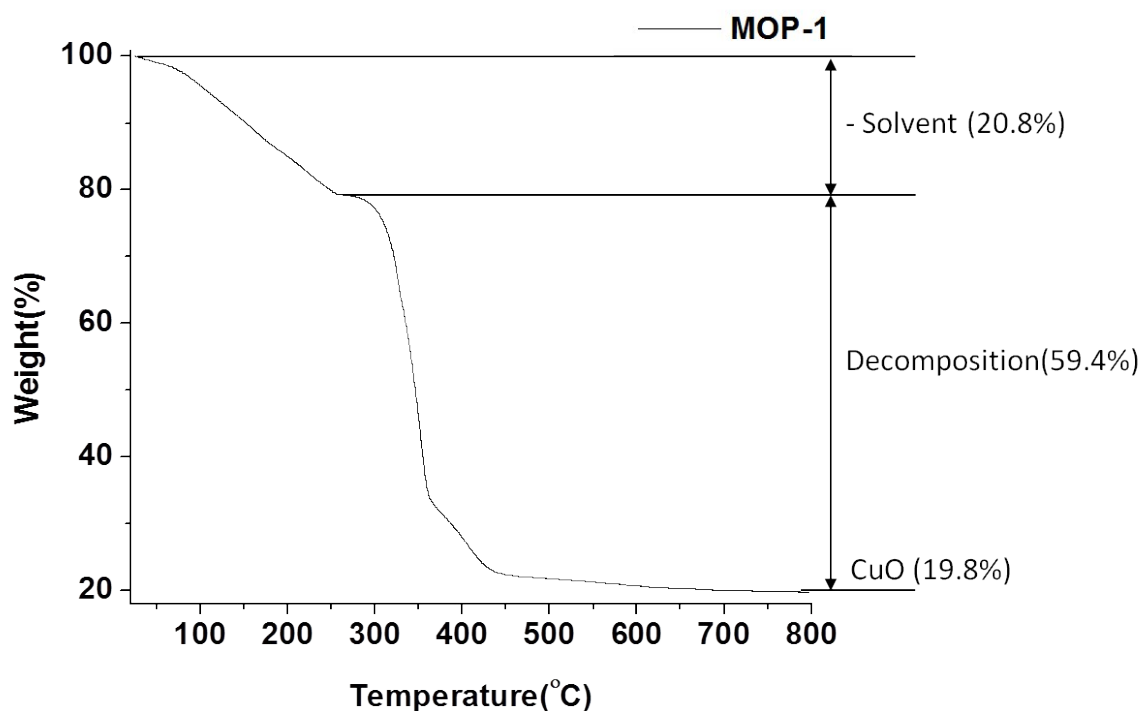


Figure S48. TGA curve of Coumarin-MOP-1.

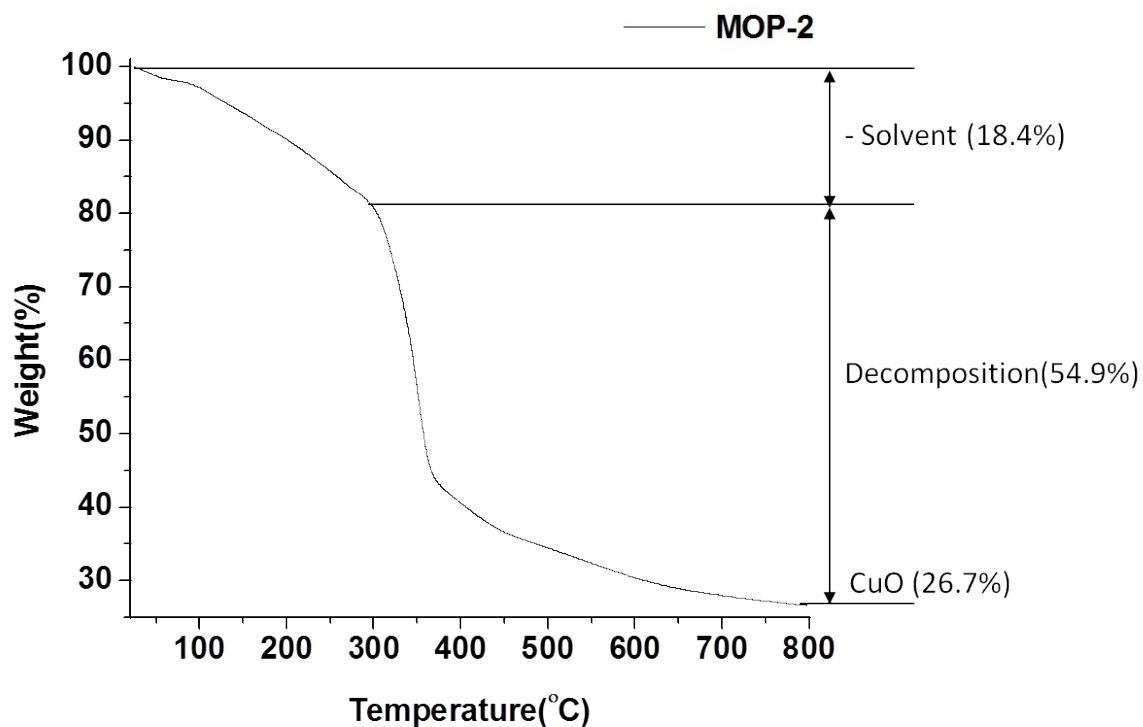
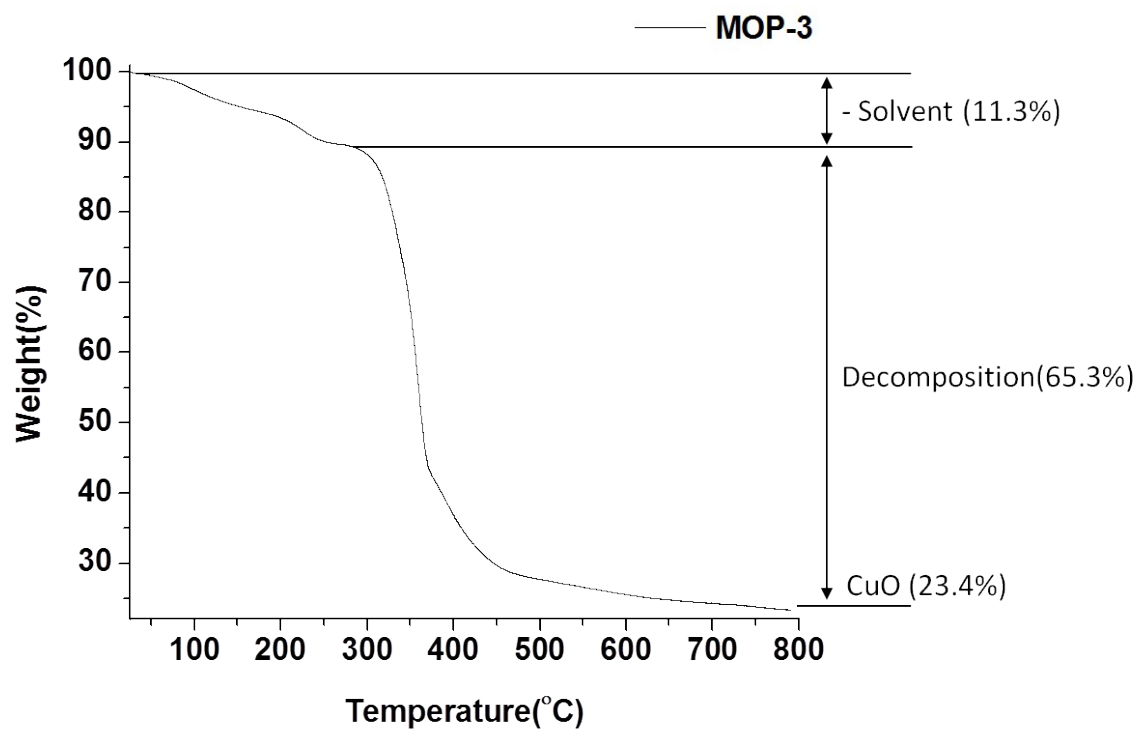


Figure S49. TGA curve of Coumarin-MOP-2.



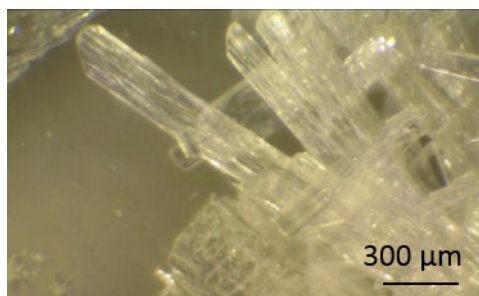
**Figure S50.** TGA curve of Coumarin-MOP-3.

## SUPPORTING INFORMATION

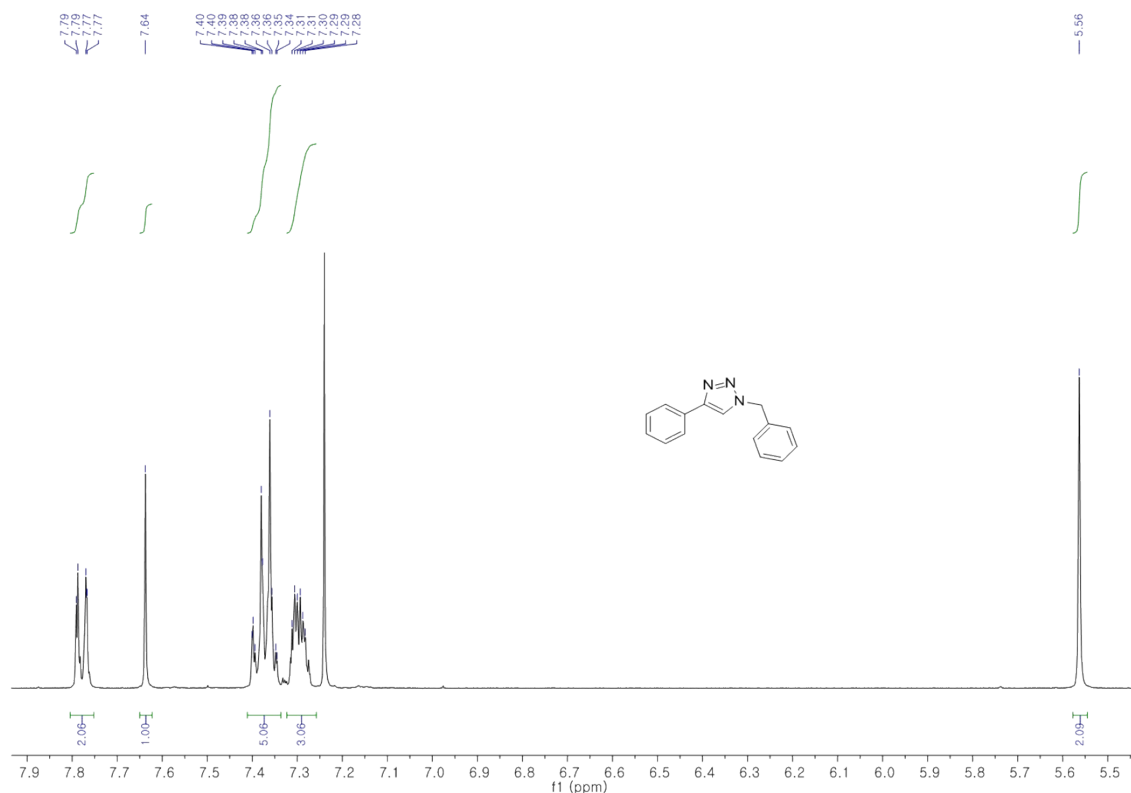
### Part S6. Copper Catalyzed Azide-Alkyne Cycloaddition (CuAAC)

#### 1. Catalytic Activity Test with Click Reaction of Coumarin-MOP-1

A solution of **L1** (0.0041 g, 0.0110 mmol) in 0.05 ml of DMF was added to a solution of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.0022 g, 0.0110 mmol) in 0.04 ml of DMF. After 1 day, benzophenone (0.0020 g, 0.0110 mmol) was dissolved in the MOP solution and 0.031 ml of methanol was added to the MOP solution. Benzyl azide (0.0293 g, 0.220 mmol) and phenylacetylene (0.0235 g, 0.230 mmol) were added to the solution and then the solution was mixed with magnetic stirring. The solution was purged with Ar gas for 30 seconds. The solution placed with UV light at 365 nm and magnetic stirring for 3 h at RT. The reaction was continued for an additional 3 h without irradiation for its completion. The solution colour was changed to yellow from orange and a white crystalline precipitate was formed in solution. The precipitate was washed with ethanol and hexane. Yield 0.0463 g (89.4%).  $^1\text{H-NMR}$  (400MHz;  $\text{CDCl}_3-d_7$ ):  $\delta$  7.78(q, 2H), 7.64(s, 1H), 7.37(m, 5H), 7.29(m, 3H), 5.56(s, 2H).



**Figure S51.** Photograph of the final product from the click reaction.



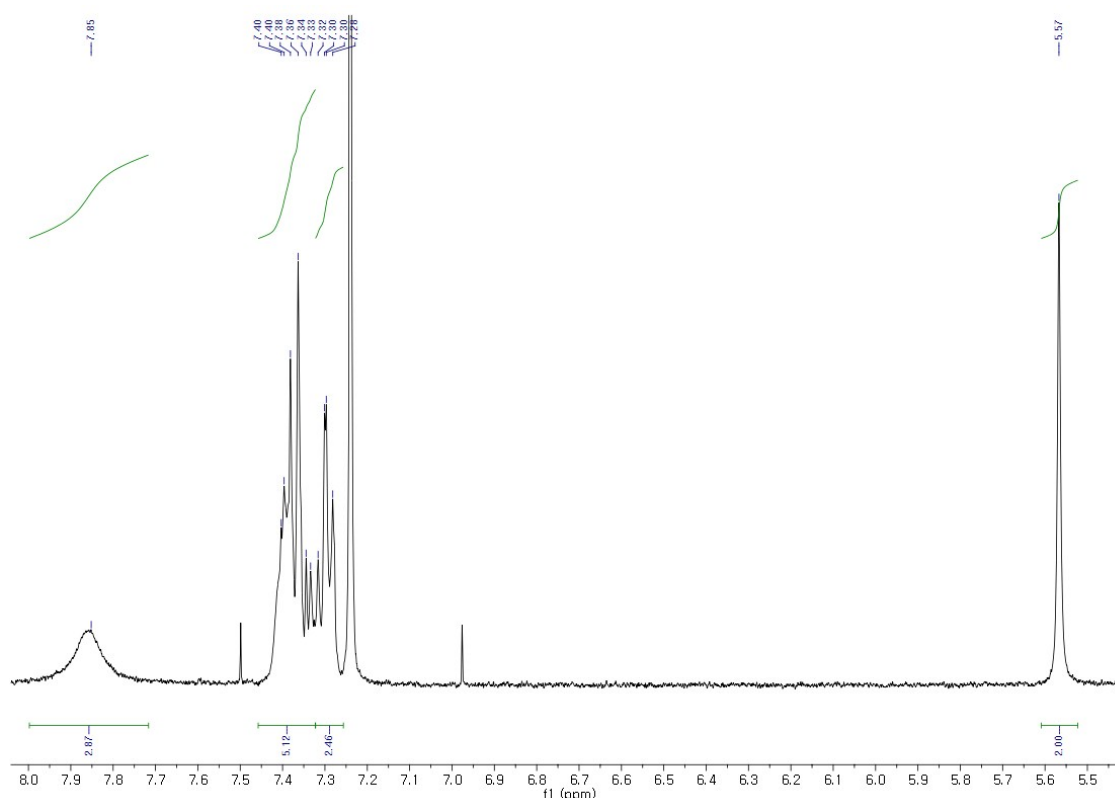
**Figure S52.**  $^1\text{H-NMR}$  analysis data of the final product from the click reaction.

## SUPPORTING INFORMATION

### 2. Catalytic Activity Test with Click Reaction of Cu<sup>+</sup> source

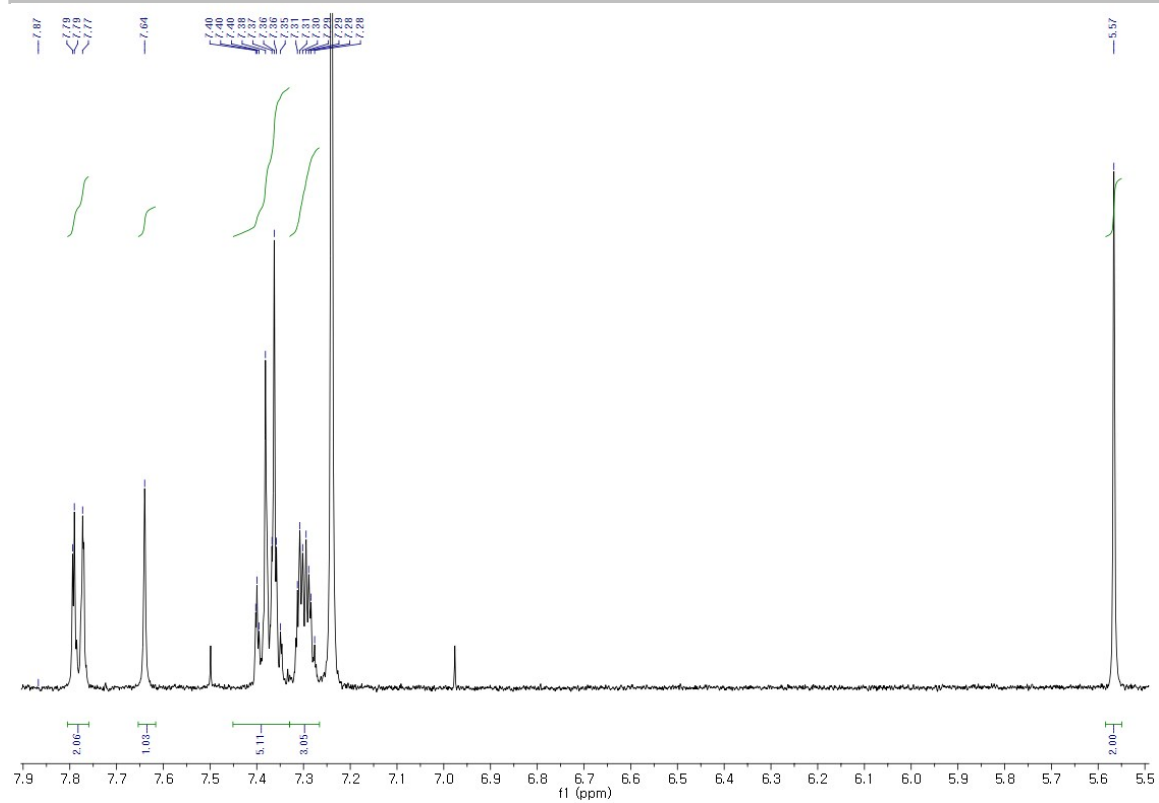
CuI (0.0021 g, 0.0110 mmol) or CuCl (0.0011g, .0110 mmol) was stirred with 0.09 ml of DMF. Benzophenone (0.0020 g, 0.0110 mmol) was dissolved in the Cu<sup>+</sup> solution and 0.031 ml of methanol was added to the Cu<sup>+</sup> solution. Benzyl azide (0.0293 g, 0.220 mmol) and phenylacetylene (0.0235 g, 0.230 mmol) were added to the solution and then the solution was mixed with magnetic stirring. The solution was purged with Ar gas for 30 seconds. The solution was placed with magnetic stirring for 3 h at RT. The solution colour was changed to yellow from orange and a white crystalline precipitate was formed in solution. The residue was dissolved in chloroform and then water (5 ml) was added. The aqueous phase was extracted three times with chloroform. The combined organic layers were dried over MgSO<sub>4</sub>. The precipitate was washed with hexane. Yield 0.0244 g from CuI (47.1%). <sup>1</sup>H-NMR (400MHz; CDCl<sub>3</sub>-d<sub>1</sub>): δ 7.85(br, 3H), 7.37(m, 5H), 7.30(m, 3H), 5.57(s, 2H).

Yield 0.0173 g from CuCl (33.4%). <sup>1</sup>H-NMR (400MHz; CDCl<sub>3</sub>-d<sub>1</sub>): δ 7.77(q, 2H), 7.64(s, 1H), 7.38(m, 5H), 7.29(m, 3H), 5.57(s, 2H).



**Figure S53.** <sup>1</sup>H-NMR analysis data of the final product from the click reaction of CuI. The low resolution of the data is resulted from the inclusion of CuI in NMR solution.

## SUPPORTING INFORMATION



**Figure S53.**  $^1\text{H-NMR}$  analysis data of the final product from the click reaction of  $\text{CuCl}$ .